Rotational analysis of the 7000 A (A 3Φ → X 3Δ) electronic emission system of diatomic vanadium mononitride (VN)

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The (0,0) band of the electronic emission system of the diatomic molecule VN at ~7000 Å has been generated and rotationally analyzed. The system is 3Φ, → 3Δ, and is the vanadium analog of the niobium nitride system centered ~6029 Å. The constants for the upper and lower (almost certainly the ground) states have been determined, including estimates of the spin–orbit coupling constants, despite the absence of satellite bands. The subband origins are somewhat asymmetrically located, probably due to the interaction of the ΛΔ 2 and the higher lying (by ~3000 cm⁻¹) ΛΔ 3 state. There is no evidence of localized perturbations in any of the subbands. VN has the shortest bond length (r₀ = 1.566 Å) observed for any diatomic molecule containing a transition metal (apart from some hydrides). The (1,1) sequence bands have also been observed but have not been rotationally analyzed at this time.

INTRODUCTION

Despite the observation of some rotational structure in the emission of active nitrogen plasmas containing volatile first row transition metal compounds 1-3 there has, so far, only been a single species (TiN) in which the emitting states of the second and third transition series metals 1-2,7-9 and of the extensive oxide systems known for all of the first row transition elements 10,11 Most of the reasons for wishing to extend information about these nitride species have been summarized recently 9 and will not be repeated here except to add the continuing interest in chemical vapor deposition (CVD) of nitride films 12-14

EXPERIMENTAL

The essential details of the generation of transition metal nitrides have been given previously 4,6 and the only difference was the use, in this study, of Kodak HSIR film which has a sufficient response in the 7000 Å region to be the emission of choice. The reference spectrum was a thorium discharge bulb containing ThI₄ which was excited by a 2.45 GHz microwave generator at a power of ~80 W.

The spectrum was recorded in the eighth and ninth orders of a 3.4 m Jarrell–Ash spectograph with reciprocal dispersions of ~6 and 3 Å per cm, respectively. Thirty thorium lines were measured and fitted to a quartic with an absolute standard deviation of 0.005 Å. The molecular lines were measured to an accuracy of ~0.01 cm⁻¹ at worst, except for badly blended lines which were discarded in the analysis if their errors were greater than 2σ.

The constants were initially obtained for each subband and then used in the usual way for a nonlinear least-squares global analysis using the methods of Zare et al. 13 and other considerations discussed previously. 9

RESULTS

The vacuum wave numbers of the 234 lines included in the analysis are given in Table I. The system constants and their error limits (in terms of 2σ where σ is the standard deviation) are given in Table II together with the values of B appropriate to each subband. A list of the wavelengths (air) of the features associated with the spectrum, both the 0,0 and the 1,1 sequences, is given in Table III.

As has been fully discussed elsewhere, 9 the absolute values of A, A J, and δ (the term asymmetry parameter) are not well determined by the final values even with inclusion of the usual 2σ errors given, but further refinement would depend upon the addition of particular kinds of new data—such as the frequencies of combination band lines—which are not yet available. Because of the asymmetry of the subband locations, i.e., the nonequality of the pure case (a) separations of the ΛΔ 2 → ΛΔ 3, ΛΦ 2 → ΛΔ 3, and ΛΦ 2 → ΛΔ 3 subbands, the parameter δ was included in two different ways. Since it is possible to estimate the ΛΔ 2 → ΛΔ 3 interaction to some precision (see below), δ was first estimated only for the ground state. Following the least-squares iteration with a frozen (0) value of δ', the upper state δ value was also allowed to float. The final constants, together with the 2σ values, pertain to this last iteration. In fact, while the standard deviation of the residuals was slightly lower for the calculation using only a single δ value (despite a correlation coefficient of 1.0000) the standard deviations obtained from the calculation using both an upper and a lower state value of δ (of course δ'–δ is constant) have been retained as those given in Table II.

This choice is, in our opinion, mandated by the unrealistically low values of 2σ given by the one-parameter model, particularly for the A values. Additionally, the error to be expected for the electronic origin, considering the errors in the A values, is almost certainly much larger than given by the nonlinear least-squares analysis, and it is unlikely to be substantiated by future refinements in the analysis. 9
TABLE II. Derived constants for the \( \Delta \) and \( \Phi \) states.

<table>
<thead>
<tr>
<th>( T^\Delta )</th>
<th>( A^\Phi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T^\phi )</td>
<td>fixed at 0</td>
</tr>
<tr>
<td>( T^\phi )</td>
<td>68 (7)</td>
</tr>
<tr>
<td>( A^\Phi )</td>
<td>0.625 38 (12)</td>
</tr>
<tr>
<td>( 10^0D )</td>
<td>0.875 (80)</td>
</tr>
<tr>
<td>( 10^0A_j )</td>
<td>-0.16 (15)</td>
</tr>
<tr>
<td>( \delta )</td>
<td>-1.1 (5)</td>
</tr>
<tr>
<td>( B_j )</td>
<td>0.620 2</td>
</tr>
<tr>
<td>( B_k )</td>
<td>-0.625 6</td>
</tr>
<tr>
<td>( B_\ell )</td>
<td>-0.630 5</td>
</tr>
</tbody>
</table>

*All units are reciprocal cm. \( T^\phi \), \( A^\Phi \), and \( B^\Phi \) are fully defined in Ref. 9 (pp. 280 and 281). The numbers in parentheses correspond to 2 standard deviations on the last digit. The rms of the residuals obtained is 0.012 cm⁻¹.

The other hand, the current values of the constants represent an excellent first-order approach to the analysis of this spectrum.

The essential quality of the analysis is also established from the \( D' \) and \( D^\Phi \) values which, taken in conjunction with the reciprocal moments and the Kratzer relationship, allow the vibrational frequencies for both the upper and lower states to be estimated. Using the calculated \( D \) values together with their error limits, the frequencies of the upper and lower states are given as 1015 ± 50 and 1070 ± 50 cm⁻¹, respectively. No progressions were observed despite a careful search, but the 1,1 sequence occurs with a separation of 55 ± 3 cm⁻¹ (dependent upon subband) and this is exactly the value predicted from the calculated upper and lower state frequencies.
TABLE III. R and Q branch heads for the 0,0 and 1,1 sequences.*

<table>
<thead>
<tr>
<th>Branch</th>
<th>F₁</th>
<th>F₂</th>
<th>F₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>R₂</td>
<td>0</td>
<td>1,1</td>
<td>0</td>
</tr>
<tr>
<td>Q₂</td>
<td>7019.41</td>
<td>7045.67</td>
<td>6972.02</td>
</tr>
</tbody>
</table>

*All values are in \( \lambda \text{(air)} \) Å.

DISCUSSION

The carrier of the spectrum has been identified since a system of bands in the region of 6200 Å had previously been observed both in emission and in chemiluminescence and its carrier determined to be VN by isotopic generation with \( ^{15}N_2 \). The \( 3\Phi_2 \rightarrow 1\Delta_2 \) subband of the system reported in this paper was shown to have the same lower state combination differences as the previously known pair of bands at \( \sim 6200 \) Å which form the \( 1\Pi_0 \rightarrow 1\Delta_1 \) subband of the VN \( 1\Pi \rightarrow 3\Delta \) emission system. The identity of the carrier as VN is thereby established. The \( 1\Pi \rightarrow 3\Delta \) system will be reported elsewhere.

At moderate resolution (\( \sim 5 \times 10^3 \)) the spectrum appears much as expected for an ordinary \( \Phi \rightarrow \Delta \) system except for significantly low intensity in the low \( J \) region of the \( R \) branch in both the highest and lowest subbands. Under higher resolution (\( \sim 5 \times 10^3 \)), it is clear that this intensity reduction is due to extensive hyperfine splitting of the \( R \) branch lines at low \( J \). This has been previously well documented and is a result of case (aβ) nuclear coupling in both the upper and lower states such that the resultant spectrum exhibits large nuclear hyperfine splitting which is inversely proportional to \( J^2 \). Under high resolution there is also evidence of significant broadening of the \( R \) and \( Q \) branch lines at high \( J \) values which is almost certainly to be associated with nuclear spin uncoupling with increasing rotation. This was also observed for NbN.

There is also one additional difference in appearance and complicating experimental factor—in the VN spectrum compared with that in NbN. In NbN the separation of the 0,0 sequence subbands is much larger than the separation between the 0,0 and 1,1 sequences, thereby reducing the line density in the regions of the \( 3\Phi_1 \rightarrow 1\Delta_1 \) and \( 3\Phi_2 \rightarrow 1\Delta_2 \) subbands. In VN there is a significant overlap of some regions of the 0,0 sequences of these two subbands with the 1,1 sequences and this has resulted in much greater difficulty in obtaining unblended \( P_1 \), \( P_2 \), and even \( P_3 \) branch lines in particular, as well as some \( R_1 \), \( R_3 \), \( Q_2 \), and \( Q_3 \) lines. Accordingly it is not possible to positively confirm the absence of any localized (rotational) perturbations with the same degree of confidence as was possible for NbN, but from a careful perusal of the data it would appear that none exists which results in systematic line shifts > 0.03 cm⁻¹.

The asymmetry of the subband separation is not as marked as in NbN. In NbN the interaction between \( 1\Delta_1 \) and \( 1\Delta_2 \) shifts the former \( \sim 33 \) cm⁻¹ to lower energies while the \( 3\Phi_3 \) level shifts the \( 3\Phi_3 \) level \( \sim 7 \) cm⁻¹ to higher energies thereby enhancing the asymmetry. It is possible to estimate the \( \Delta_a \rightarrow \Delta_b \) separation using the principles given previously and it is clear that their separation (\( \Delta \)) is such that \( 3500 > \Delta > 2500 \) cm⁻¹. The upper and lower bounds lead to a shift parameter (\( \delta \)) such that \( 10 > \delta > 3 \) cm⁻¹. The shift parameter for the \( 3\Phi_3 \) levels is much more difficult to estimate due to significant uncertainties as to their energy separation. It was for this reason that, initially, only \( \delta \) was used in the least-squares analysis.

The initial values of \( A' \) and \( A'' \) (80 and 70 cm⁻¹, respectively) were estimated from atomic spectra and, while the final values as given in Table II are not expected to be the best values obtainable in the future, they are probably correct within the wide error limits given. This comment is supported by the fact that from them it is possible to calculate \( a_n \) and \( a_\alpha \) and then calculate \( A \) for the related \( 3\Pi \) state, which is expected to lie at higher energies than the \( 3\Phi \) level (which has been located and analyzed in NbN). The result yields \( A_{1\Pi} \approx 40 \) cm⁻¹ and, taken in conjunction with the spin–orbit splitting of the \( \Delta \) state, leads to the prediction of a 100 cm⁻¹ separation between the three components of the \( 3\Pi \rightarrow X^3\Delta \) transition. As a result of this calculation it has been possible to locate these components and, indeed, their subband spacing is \( \sim 100 \) cm⁻¹ with \( 3\Pi \rightarrow 1\Delta_1 \) at the highest frequency. The complete rotational analysis will be given elsewhere.

As mentioned above, there is considerable hyperfine splitting in the low \( J \) lines of all branches in both the \( 3\Phi_3 \rightarrow 1\Delta_3 \) and \( 3\Phi_2 \rightarrow 1\Delta_2 \) subbands so that lines with \( J < 8 \) are greatly broadened or split into distinct hyperfine components. Due to large contaminating line densities in the relevant regions, an unambiguous analysis of the hyperfine split lines must await further study at considerably higher (sub-Doppler) resolving powers.

Finally, it is of considerable interest to note that the internuclear separation \( (r) \) in the \( (X) \) \( 3\Sigma \) state is 1.566 Å, a remarkably short bond. It is the shortest bond distance recorded for any diatomic molecule containing a transition metal (or even a nontransition metal) and an element other than hydrogen. The distance is almost the same as for LiF and somewhat shorter than for SiO and ZnO which has an \( r \) of 1.5719 Å. By now a considerable number of internuclear distances for oxides and nitrides are known for the first and second transition metal oxide and nitride molecules of the first and second transition series.

TABLE IV. Bond lengths for the low lying electronic states of the 1-e, 2-e, and 3-e transition metal oxide and nitride molecules of the first and second transition series.*

<table>
<thead>
<tr>
<th>Term</th>
<th>Oxide</th>
<th>Nitride</th>
<th>Oxide</th>
<th>Nitride</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^3\Sigma (\sigma') )</td>
<td>ScO, 1.668</td>
<td>TiN, 1.583</td>
<td>YO, 1.790</td>
<td>ZrN, 1.679</td>
</tr>
<tr>
<td>( ^3\Delta (\delta') )</td>
<td>TiO₂, [1.620]</td>
<td>VN, 1.566</td>
<td>ZrO₂, [1.279]</td>
<td>NbN, 1.662</td>
</tr>
<tr>
<td>( ^2\Sigma (\sigma') )</td>
<td>TiO₂, [1.600]</td>
<td>VN, 1.586</td>
<td>ZrO₂, [1.712]</td>
<td>NbN, 1.651</td>
</tr>
<tr>
<td>( ^2\Sigma (\delta') )</td>
<td>VO, 1.592</td>
<td>CrN, …</td>
<td>NbO, 1.691</td>
<td>MoN, 1.636</td>
</tr>
</tbody>
</table>

*� indicates that these are \( r \) values. All other distances are \( r_\alpha \) (Å).
second transition series metals, and they are given in Table IV. In this table it is not indicated which terms constitute the ground state (for the 2-e configurations) but it is clear from the figures that as far as the internuclear distances are concerned it is not relevant. Thus, for TiO and NbN, the ground term is $3\Delta$ and yet the internuclear distances for the $1\Sigma^+$ terms are less than for $3\Delta$. In ZrO the ground term is the $1\Sigma$ which also has a smaller $r_0$ than for $3\Delta$.

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