Rotational analysis of the 7000 Å ($A\ ^3\Phi \rightarrow X\ ^3\Delta$) electronic emission system of diatomic vanadium mononitride (VN)

S. L. Peter[a] and T. M. Dunn[b]
Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109

(Received 26 August 1988; accepted 8 February 1989)

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 $^3\Phi_r \rightarrow {}^3\Delta_r$ 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 $^3\Delta_2$ and the higher lying (by ~3000 cm^{-1}) $^1\Delta_2$ state. There is no evidence of localized perturbations in any of the subbands. VN has the shortest bond length ($r_0 = 1.566$ 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 have been positively identified.[4-6] This situation is somewhat surprising in view of the much greater success obtained for nitrides 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[4,9] 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 emulsion of choice. The reference spectrum was a thorium discharge bulb containing ThI_4 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 spectrograph 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.*[15] 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 $^3\Phi_4 \rightarrow {}^3\Delta_3$, $^3\Phi_3 \rightarrow {}^3\Delta_2$, and $^3\Phi_2 \rightarrow {}^3\Delta_1$ subbands, the parameter δ was included in two different ways. Since it is possible[9,16] to estimate the $^3\Delta_2$–$^1\Delta_2$ 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] On the

[a] Present address: Department of Chemistry, Washington State University, Pullman, Washington 99164.
[b] To whom all correspondence should be addressed.

 0021-9606/89/105333-04$02.10 © 1989 American Institute of Physics

TABLE I. Line frequencies for the 0,0 sequence.

$F_1(J)$				$F_2(J)$				$F_3(J)$			
J	R branch	Q branch	P branch	J	R branch	Q branch	P branch	J	R branch	Q branch	P branch
2				2	14 317.368			2			
3				3	14 318.502			3			
4				4	14 319.616			4			
5				5	14 320.695			5			
6	14 220.412			6	14 321.725	14 313.169		6	14 412.433		
7	14 221.442			7	14 322.738	14 312.972		7	14 413.412		
8	14 222.473	14 211.512		8	14 323.720	—	14 302.934	8	14 414.382	14 403.334	14 393.480
9		14 211.308	14 200.329	9	14 324.662	14 312.452	—	9	14 415.333	14 403.017	14 391.989
10	14 224.423	14 211.080	—	10	14 325.587	14 312.149	14 299.924	10	14 416.193	14 402.704	14 390.407
11	14 225.372	14 210.796	14 197.451	11	14 326.474	14 311.823	—	11	14 417.064	14 402.334	14 388.829
12	14 226.312	14 210.506	14 195.927	12	14 327.334	14 311.469	—	12	14 417.887	14 401.938	14 387.209
13	14 227.210	14 210.206	—	13	14 328.168	14 311.076	—	13	14 418.689	14 401.513	14 385.542
14	14 228.107	14 209.855	14 192.851	14	14 328.958	14 310.663	14 293.571	14	14 419.459	14 401.045	14 383.844
15	14 228.968	14 209.490	14 191.275	15	14 329.737	14 310.199	14 291.907	15	14 420.179	14 400.545	14 382.150
16	14 229.761	14 209.118	14 189.676	16	14 330.479	14 309.741	—	16	14 420.860	14 400.013	14 380.370
17	14 230.568	14 208.706	14 188.034	17	14 331.190	14 309.223	14 288.471	17	14 421.537	14 399.443	—
18	14 231.341	14 208.277	14 186.391	18	14 331.866	14 308.689	14 286.762	18	14 422.151	14 398.841	14 376.750
19	14 232.103	14 207.800	—	19	14 332.515	14 308.136	14 284.949	19	14 422.740	14 398.227	14 374.917
20	14 232.815	14 207.328	14 183.031	20	14 333.151	14 307.531	14 283.118	20	14 423.308	14 397.549	14 373.037
21	—	14 206.806	14 181.310	21	14 333.733	14 306.900	14 281.282	21	14 423.835	14 396.853	14 371.131
22	14 234.224	14 206.279	14 179.563	22	14 334.292	14 306.246	14 279.396	22	14 424.330	14 396.129	14 369.179
23	14 234.868	14 205.708	—	23	14 334.837	14 305.581	14 277.521	23	14 424.781	14 395.364	14 367.200
24	14 235.477	14 205.130	14 176.002	24	14 335.316	14 304.843	—	24	14 425.216	14 394.564	14 365.147
25	14 236.068	14 204.527	14 174.178	25	14 335.794	14 304.112	14 273.601	25	14 425.597	14 393.731	14 363.080
26	14 236.656	14 203.889	14 172.336	26	14 336.220	14 303.322	14 271.640	26	14 425.959	14 392.874	—
27	—	14 203.220	14 170.468	27	14 336.630	14 302.505	14 269.607	27	14 426.288	14 391.989	14 358.921
28	14 237.699	14 202.543	14 168.612	28	14 336.993	14 301.679	14 267.544	28	14 426.581	14 391.060	14 356.776
29	14 238.230	14 201.832	—	29	14 337.359	14 300.808	—	29	14 426.816	14 390.098	14 354.577
30	14 238.672	14 201.086	14 164.713	30	14 337.645	14 299.924	14 263.374	30	14 427.050	14 389.100	14 352.380
31	14 239.110	14 200.329		31	14 337.957	14 298.984	14 261.223	31	14 427.221	14 388.069	
32	—	14 199.553		32	14 338.232	14 298.037	14 259.072	32	14 427.373	14 387.016	
33	14 239.920	14 198.730		33	14 338.444	14 297.048	14 256.872	33		14 385.919	
34	14 240.320	14 197.871		34	14 338.635	14 296.007		34		14 384.799	
35	—	14 197.027		35	14 338.787	14 294.967		35		14 383.651	
36	14 240.966	—		36	14 338.917	14 293.902		36		14 382.449	
37		14 195.218		37		14 292.788		37		14 381.228	
38		14 194.255		38		14 291.653		38		14 379.951	
39		14 193.303		39		14 290.486		39		—	
40		14 192.309		40		14 289.289		40		14 377.354	
41		14 191.275		41		14 288.071		41		14 375.995	
42		14 190.250		42		14 286.762		42			
43		14 189.203		43		14 285.520		43			
44		14 188.108		44		14 284.198		44			
45				45		14 282.864		45			
46				46		14 281.468		46			
47				47		14 280.054		47			

TABLE II. Derived constants for the $X\,^3\Delta$ and $A\,^3\Phi$ states.[a]

	$X\,^3\Delta$	$A\,^3\Phi$
T_0^*	fixed at 0	14 313.247(4)
A^*	68(7)	78(5)
B^*	0.625 38(12)	0.610 85(13)
$10^6 D$	0.875(80)	0.915(80)
$10^3 A_J$	− 0.16(15)	− 0.06(4)
δ	− 5.4(5)	~0(5)
B_1	0.620 2	0.608 1
B_2	0.625 6	0.613 9
B_3	0.630 5	0.631 9

[a] All units are reciprocal cm. T_0^*, A^*, and B^* 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}.

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'' 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 $1070 \pm 50\ cm^{-1}$, respectively. No progressions were observed despite a careful search, but the 1,1 sequence occurs with a separation of $55 \pm 3\ cm^{-1}$ (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.[a]

	F_1		F_2		F_3	
Branch	0,0	1,1	0.0	1,1	0.0	1,1
R_i	7019.41	7045.67	6972.02	7001.17	6929.23	6958.18
Q_i	7034.12	···	6984.49	7010.49	6940.93	6969.5

[a] All values are in λ(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[1] and in chemiluminescence[17] and its carrier determined to be VN by isotopic generation with $^{15}N_2$ (95%). The $^3\Phi_2 \rightarrow {}^3\Delta_1$ 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 ~6200 Å which form the $^3\Pi_0 \rightarrow {}^3\Delta_1$ subband of the VN $^3\Pi \rightarrow {}^3\Delta$ emission system. The identity of the carrier as VN is thereby established. The $^3\Pi \rightarrow {}^3\Delta$ system will be reported elsewhere.[18]

At moderate resolution ($\sim 5\times 10^4$) the spectrum appears much as expected for an ordinary $^3\Phi \rightarrow {}^3\Delta$ system[19] except for significantly low intensity in the low J region of the R branch in both the highest and lowest subbands. Under higher resolution ($\sim 5\times 10^5$), 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[20–22] and is a result of case ($a\beta$) nuclear coupling in both the upper and lower states such that the resultant spectrum exhibits large nuclear hyperfine splitting[23] 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[9] 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 $^3\Phi_3 \rightarrow {}^3\Delta_2$ and $^3\Phi_2 \rightarrow {}^3\Delta_1$ 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_2, R_3, Q_2, and Q_3 lines. Accordingly it is not possible[9] 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[9] as in NbN. In NbN the interaction between $^3\Delta_2$ and $^1\Delta_2$ shifts the former ~33 cm^{-1} to lower energies while the $^1\Phi_3$ level shifts the $^3\Phi_3$ level ~7 cm^{-1} to *higher* energies thereby enhancing the asymmetry.[9] It is possible to estimate the $^3\Delta_2$–$^1\Delta_2$ separation using the principles given previously,[9,16] and it is clear that their separation (Δ) is such that $3500 > \Delta > 2500$ (cm^{-1}). The upper and lower bounds lead to a shift parameter[9] (δ) such that $10 > \delta'' > 3$ (cm^{-1}). The shift parameter for the $^1\Phi_3$ and $^3\Phi_3$ levels is much more difficult to estimate due to significant uncertainties as to their energy separation. It was for this reason that, initially, only δ'' 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[9] 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_π and a_δ and then calculate A for the related $^3\Pi$ state, which is expected to lie at higher energies than the $^3\Phi$ level (and which has been located and analyzed[2] in NbN). The result yields $A_{II} \sim 40$ cm^{-1} and, taken in conjunction with the spin–orbit splitting of the $^3\Delta$ 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 ~100 cm^{-1} with $^3\Pi_0 \rightarrow {}^3\Delta_1$ at the highest frequency. The complete rotational analysis will be given elsewhere.[18]

As mentioned above, there is considerable hyperfine splitting in the low J lines of all branches in both the $^3\Phi_4 \rightarrow {}^3\Delta_3$ and $^3\Phi_2 \rightarrow {}^3\Delta_1$ subbands so that lines with $J \leqslant 8$ 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_0) in the $(X)^3\Delta$ 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.[11] The distance is almost the same[11] as for LiF and somewhat shorter than for SiN($X\,^2\Sigma$) which has an r_e of 1.5719 Å. By now a considerable number of internuclear distances for oxides and nitrides are known for the first and

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.[a]

	First transition series		Second transition series	
Term	Oxide	Nitride	Oxide	Nitride
$^2\Sigma(\sigma^1)$	ScO, 1.668	TiN,1.583	YO, 1.790	ZrN, 1.697
$^3\Delta(\delta^1\sigma^1)$	TiO,[1.620]	VN , 1.566	ZrO, [1.729]	NbN, 1.662
$^1\Sigma(\sigma^2)$	TiO,[1.600]	VN, ···	ZrO, [1.712]	NbN, 1.651
$^4\Sigma(\sigma^1\delta^2)$	VO, 1.592	CrN, ···	NbO, 1.691	MoN, 1.636

[a] [ ] indicates that these are r_e (Å) values. All other distances are r_0 (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 the $^3\Delta$. In ZrO the ground term is the $^1\Sigma$ which also has a smaller r_0 than for $^3\Delta$.

ACKNOWLEDGMENT

One of us (T.M.D.) is indebted to the PS and SW Company for the support of this project.

[1]J. K. Bates, Ph.D. thesis, University of Michigan, 1975.
[2]N. L. (Ranieri) Klymko, Ph.D. thesis, University of Michigan, 1979.
[3]D. Van Vechten, N. Bauer, R. Cusick, and T. M. Dunn, J. Phys. Chem. **85**, 1559 (1985).
[4]T. M. Dunn, L. K. Hanson, and K. A. Rubinson, Can. J. Phys. **48**, 1657 (1970).
[5]J. K. Bates, N. Ranieri, and T. M. Dunn, Can. J. Phys. **54**, 915 (1976).
[6]C. Athénour, J-L. Féménias, and T. M. Dunn, Can. J. Phys. **60**, 109 (1982).
[7]J. K. Bates and T. M. Dunn, Can. J. Phys. **54**, 1216 (1976).
[8]R. Carlson, J. K. Bates, and T. M. Dunn. J. Mol. Spectrosc. **110**, 215 (1985).
[9]J.-L. Féménias, C. Athénour, K. M. Rao, and T. M. Dunn, J. Mol. Spectrosc. **130**, 269 (1988).
[10]A. Gatterer, J. Junkes, E. W. Salpeter, and B. Rosen, Molecular Spectra of Metallic Oxides, Specola Vaticana (1957).
[11]K.-P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules* (Van Nostrand, New York, 1979).
[12]C. Y. Ting, J. Vac. Sci. Technol. **21**, 14 (1982).
[13]L. Roux, J. Hanus, J.C. Francois, and M. Sigrist, Solid Energy Mater. **7**, 299 (1982).
[14]S. R. Kurtz and R. G. Gordon, Thin Solid Films **140**, 277 (1986).
[15]R. N Zare, A. L. Schmeltekopf, W. J. Harrop, and D. L. Albritton, J. Mol. Spectrosc. **46**, 37 (1973).
[16]T. M. Dunn (unpublished work).
[17]D. Van Vechten, N. Bauer, R. Cusick, and T. M. Dunn, J.Phys. Chem. **85**, 1559 (1985).
[18]J. K. Bates, M. Mandich, S. L. Peter, N. L. Klymko, and T. M. Dunn (to be submitted).
[19]J. A. Phillips, Astrophys. J. **114**, 152 (1951).
[20]T. M. Dunn and K.M. Rao, Nature **222**, 266 (1969).
[21]T. M. Dunn, in *Molecular Spectroscopy: Modern Research* (Academic, New York, 1972).
[22]J.-L. Féménias, C. Athénour, and T. M. Dunn, J. Chem. Phys. **63**, 2861 (1975).
[23]R. A. Frosch and H. M. Foley, Phys. Rev. **88**, 1337 (1952).