Journal of Molecular Spectroscopy **215,** 163–164 (2002)
doi:10.1006/jmsp.2002.8617

NOTE

Fourier Transform Emission Spectroscopy of the $f\,^1\Phi$–$a\,^1\Delta$ System of VN

The visible spectra of VN have been known since 1989, when Peter and Dunn (*1*) observed the emission spectrum of the $A^3\Phi$–$X^3\Delta$ transition near 700 nm. In the same year, Simard *et al.* (*2*) observed VN in a molecular beam using the laser vaporization technique and observed three transitions, $^3\Phi$–$^3\Delta$, $^3\Pi$–$^3\Delta$, and $^1\Sigma^+$–$^3\Delta_1$, with 0–0 bands near 700, 624, and 616 nm, respectively. Simard *et al.* (*2*) provided the gas phase ground state vibrational interval of 1020 ± 5 cm^{-1} and also reported a rotational analysis of the 0–0 band of the $^1\Sigma^+$–$^3\Delta_1$ intercombination transition. They labeled this transition as $d^1\Sigma^+$–$X^3\Delta_1$. The 624-nm transition was later studied at sub-Doppler resolution by Balfour *et al.* (*3*), who labeled it as $D^3\Pi$–$X^3\Delta$. Balfour *et al.* (*3*) provided precise rotational and hyperfine constants for the $D^3\Pi$ and $X^3\Delta$ states. In a very recent work the present authors have investigated the emission spectra of VN in the region 3400–19 400 cm^{-1} (*4*) and observed two new singlet electronic transitions, $e^1\Pi$–$a^1\Delta$ and $d^1\Sigma^+$–$b^1\Sigma^+$, in addition to the $d^1\Sigma^+$–$X^3\Delta_1$ and the triplet–triplet transitions observed by previous workers (*1–3*).

Andrews and co-workers (*5, 6*) studied the reaction of laser-ablated first-row transition metal atoms with N_2 and observed the matrix spectra for molecules such as MN and MN_2. A sharp VN peak at 1026.2 cm^{-1} observed in solid argon was assigned as the fundamental vibrational band of VN, in agreement with the gas phase value of Simard *et al.* (*2*). The spectroscopic properties of the low-lying electronic states of VN have also been calculated by Mattar and Doleman (*7*) and more recently by Harrison (*8*). Harrison (*8*) has predicted the spectroscopic properties of most of the low-lying singlet and triplet states using MCSCF and multireference CI *ab initio* calculations.

In this paper we report the observation of another transition, $f^1\Phi$–$a^1\Delta$, in the singlet manifold near 17 432 cm^{-1}. This transition appears with very weak intensity. The experimental details are provided in our previous papers on VN (*4*) and VO (*9*), which are based on the same data. The spectra were recorded with the 1-m Fourier transform spectrometer associated with the McMath–Pierce telescope of the National Solar Observatory at Kitt Peak. The spectra were calibrated using the measurements of the $d^1\Sigma^+$–$X^3\Delta_1$ transition (*2*). The molecular lines of the $f^1\Phi$–$a^1\Delta$ transition of VN have a typical width of 0.06 cm^{-1} and appear with a maximum signal-to noise ratio of 5 : 1, so the line positions are expected to be accurate to about ± 0.003 cm^{-1}.

The spectra were measured using a program called PC-DECOMP developed by J. Brault at Kitt Peak. The peak positions were determined by fitting a Voigt lineshape function to each spectral feature and the branches were sorted using a color Loomis–Wood program running on a PC computer. The structure of the new band consists of single R, single P, and single Q branches with the Q branch being the most intense, as shown in Fig. 1. The rotational numbering was straightforward since the lower state combination differences match very well with the corresponding values from the $e^1\Pi$–$a^1\Delta$ transition (*4*). Rotational lines up to $R(44)$, $Q(50)$, and $P(47)$ were identified in the 0–0 band. The rotational structure of this band was found to be free from local perturbations. The 1–1 and higher vibrational bands of the $\Delta v = 0$ sequence, as well as any off-diagonal bands, were not observed, making it impossible to determine the equilibrium vibrational or rotational constants.

Although the first lines were not identified due to overlapping near the head, there is no doubt in the assignment of the new transition because its lower state is in common with the $e^1\Pi$–$a^1\Delta$ transition measured previously (*4*). The rotational analysis of the $f^1\Phi$–$a^1\Delta$ transition is also secure because of the presence of the Q branch. The observed line positions of the $f^1\Phi$–$a^1\Delta$ transitions of VN are provided in Table 1. The molecular constants were determined by fitting the

TABLE 1
Observed Line Positions (in cm^{-1}) for the 0–0 band of the $f^1\Phi$–$a^1\Delta$ Transition of VN

J	$R(J)$	O-C	$Q(J)$	O-C	$P(J)$	O-C
5			17431.756	−0.013		
6			17431.552	0.001		
7			17431.297	−0.001		
8			17430.995	−0.013		
9			17430.673	−0.009	17419.574	−0.011
10			17430.332	0.012	17417.988	−0.002
11			17429.932	0.011		
12	17445.495	−0.016	17429.489	0.003		
13	17446.267	−0.003	17429.022	0.008	17412.980	−0.010
14	17446.987	−0.005	17428.513	0.007	17411.255	0.006
15	17447.667	−0.010	17427.965	0.004	17409.482	0.009
16	17448.319	−0.005	17427.382	0.004	17407.666	0.005
17	17448.939	0.005	17426.763	0.004	17405.809	−0.004
18	17449.513	0.006	17426.112	0.009	17403.928	0.001
19	17450.052	0.009	17425.413	0.002	17401.992	−0.014
20	17450.533	−0.008	17424.690	0.010	17400.045	−0.002
21	17450.997	−0.003	17423.908	−0.005	17398.061	0.008
22	17451.419	−0.003	17423.099	−0.008	17395.997	−0.023
23	17451.800	−0.005	17422.270	0.004		
24	17452.148	−0.002	17421.385	−0.001		
25	17452.460	0.002	17420.464	−0.004	17389.710	0.008
26	17452.712	−0.014	17419.497	−0.015	17387.527	0.005
27	17452.950	−0.005	17418.512	−0.007	17385.289	−0.015
28	17453.139	−0.007	17417.481	−0.005	17383.041	−0.008
29	17453.306	0.009	17416.413	−0.003	17380.738	−0.018
30			17415.303	−0.004	17378.431	0.005
31			17414.149	−0.011	17376.061	0.003
32			17412.980	0.006	17373.656	0.004
33	17453.503	−0.004	17411.754	0.006	17371.200	−0.007
34	17453.457	−0.004	17410.481	−0.003	17368.725	0.001
35	17453.386	0.013	17409.179	−0.001	17366.206	0.003
36	17453.243	−0.002	17407.840	0.003	17363.636	−0.008
37	17453.080	0.004	17406.463	0.010	17361.048	0.003
38	17452.872	0.006	17405.042	0.011	17358.403	−0.005
39	17452.626	0.010	17403.566	−0.001	17355.735	0.004
40	17452.326	0.002	17402.066	0.002	17353.020	0.005
41	17451.991	0.001	17400.515	−0.005	17350.254	−0.005
42	17451.620	0.006	17398.932	−0.002	17347.475	0.011
43	17451.185	−0.010	17397.299	−0.010	17344.648	0.018
44	17450.741	0.007	17395.631	−0.011	17341.763	0.009
45			17393.927	−0.006	17338.857	0.018
46			17392.189	0.007	17335.882	−0.002
47			17390.381	−0.009	17332.899	0.012
48			17388.554	−0.001		
49			17386.672	−0.006		
50			17384.736	−0.022		

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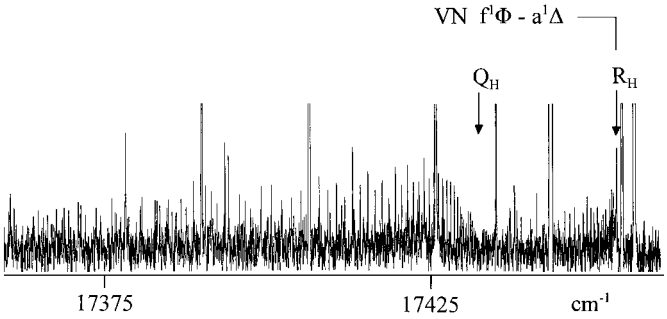

FIG. 1. A portion of the 0–0 band of the $f^1\Phi$–$a^1\Delta$ transition of VN near the *R* head.

observed line positions with the customary energy level expression:

$$F_v(J) = T_v + B_v J(J+1) - D_v[J(J+1)]^2. \quad [1]$$

The lines were weighted based on their intensity and extent of blending. The lines of the $e^1\Pi$–$a^1\Delta$ transition were also included in the final fit in order to obtain an improved set of lower state constants. The molecular constants obtained from the final fit are provided in Table 2.

The observation and assignment of the new transition are consistent with the previous *ab initio* calculation of Harrison (*8*) and fit well in the energy level diagram of the low-lying electronic states of VN (*4*) and isovalent NbN (*10, 11*). The excited state rotational constant $B_0 = 0.616718(23)$ cm^{-1} provides a bond length of $r_0 = 1.577526(29)$ Å, to be compared with the theoretical value of 1.594 Å obtained in the *ab initio* calculation of Harrison (*8*). Although the observation of this new transition combined with the transitions reported in our previous paper (*4*) provides a much better understanding of the low-lying electronic states of VN, the term values of the $a^1\Delta$, $e^1\Pi$, and $f^1\Phi$ states relative to the ground state remain unknown. Further experimental work, therefore, is needed to provide a complete picture of the low-lying electronic states of VN, as has been obtained in the case of NbN (*10, 11*).

TABLE 2
Molecular Constants (in cm^{-1}) for the $a^1\Delta$ and $f^1\Phi$ States of VN

State	T_0	B_0	$10^6 \times D_0$
$f^1\Phi$	$a + 17432.3109(16)$	0.616718(23)	1.1284(90)
$a^1\Delta$	a	0.634792(23)	0.9033(89)

Note. Numbers in parentheses are one standard deviation in the last digits quoted and "*a*" marks unknown term value of the $a^1\Delta$ state.

ACKNOWLEDGMENTS

The National Solar Observatory is operated by the Association of Universities for Research in Astronomy, Inc., under contract with the National Science Foundation. We thank J. Wagner and C. Plymate of the National Solar Observatory for assistance in obtaining the spectra. The research described here was supported by funding from the NASA laboratory astrophysics program. Support was also provided by the Natural Sciences and Engineering Research Council of Canada.

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Received May 30, 2002