# Infrared emission spectroscopy of the $[10.5]^5\Delta - X^5\Delta$ system of VF

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The emission spectrum of VF has been investigated in the 3400–17 000 cm$^{-1}$ region using a Fourier transform spectrometer. The bands were excited in a high temperature carbon tube furnace from the reaction of vanadium metal vapor with CF$_4$, as well as in a microwave discharge through a flowing mixture of VF$_4$ vapor and helium. Several bands observed in the 9000–12 000 cm$^{-1}$ region have been attributed to VF. The bands with high wave number $R$ heads near 9156.8, 9816.4, 10 481.4, 11 035.8, and 11 587.2 cm$^{-1}$ have been assigned as the 0-2, 0-1, 0-0, 1-0, and 2-0 bands, respectively, of the new $[10.5]^5\Delta - X^5\Delta$ system of VF. A rotational analysis of the $^5\Delta_1 - ^5\Delta_1$, $^5\Delta_2 - ^5\Delta_2$, $^5\Delta_3 - ^5\Delta_3$, and $^5\Delta_4 - ^5\Delta_4$ subbands of the 0-1, 0-0, 1-0, and 2-0 bands has been carried out and spectroscopic parameters for VF have been obtained for the first time. The following equilibrium constants have been determined for the ground state of VF by averaging the constants of the different spin components: $\Delta G(1/2) = 665.10$ cm$^{-1}$, $B_e = 0.3863$ cm$^{-1}$, $\alpha_e = 0.0028$ cm$^{-1}$, and $r_e = 1.7758$ Å. © *2002 American Institute of Physics.*
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## INTRODUCTION

Spectroscopic studies of transition metal-containing molecules provide insight into chemical bonding in simple metal systems.[1] Because of the high cosmic abundance of transition metal elements in stars, transition metal-containing molecules are of astrophysical importance.[2,3] While many of the diatomic transition metal oxides[4] and hydrides[5] have been relatively well characterized, and many of the nitrides have recently been investigated,[6,7] only a few transition metal halides have been studied so far. In the group V transition metal family only limited spectroscopic data are available for TaCl,[8] VCl,[9] and VF[10] from previous low resolution studies. The TaCl bands were observed from the microwave excitation of a mixture of TaCl$_4$ vapor, N$_2$, and He during a search for TaN bands, and were left unassigned.[8] The visible bands of VCl are also known[9] but their rotational analysis is still lacking. However, in a recent study of VCl we have observed a complex $^5\Delta - ^5\Delta$ transition in the near infrared which has been labeled as the $[7.0]^5\Delta - X^5\Delta$ transition[11] and we have determined the spectroscopic constants from the rotational analysis of a few bands. A number of low resolution emission bands of VF have also been observed in the visible region by Jones and Krishnamurty[10] and the electronic assignments of $^5\Sigma - ^5\Pi$ or $^5\Delta - ^5\Pi$ have been proposed. No rotational analysis of any VF bands has been reported to date.

Several theoretical studies of the spectroscopic properties of VF[12,13] and the related molecule VH[14] have been carried out in recent years. Averyanov and Khait[12] have performed an *ab initio* calculation of the spectroscopic properties of the low-lying quintet states of VF and proposed a $^5\Delta$ ground state. In another *ab initio* study, the spectroscopic properties for the low-lying electronic states of VF have been predicted by Harrison.[13] In this study, the ground state of VF was predicted to be either a $^5\Delta$ or a $^5\Pi$ state but no definite conclusion was drawn.[13] However, a $^5\Delta$ ground state has been predicted for VH by Bruna *et al.*[14] on the basis of a high quality *ab initio* calculation. Transition metal halides are expected to have a similar electronic structure as the corresponding hydrides, so that $^5\Delta$ ground states are expected for VF and VCl based on the available results for VH.[14]

In the present work we report on the observation of a new $\Delta\Omega = 0$ transition of VF in the 9000–12 000 cm$^{-1}$ region. The 0-0 band is located near 10 481 cm$^{-1}$, so this transition has been labeled as $[10.5]^5\Delta - X^5\Delta$ on the basis of a rotational analysis of the $^5\Delta_1 - ^5\Delta_1$, $^5\Delta_2 - ^5\Delta_2$, $^5\Delta_3 - ^5\Delta_3$, and $^5\Delta_4 - ^5\Delta_4$ subbands of the 0-1, 0-0, 1-0, and 2-0 bands. The $^5\Delta_{0\pm} - ^5\Delta_{0\pm}$ subband could not be identified in our spectra because of extensive overlapping from the other subbands.

## EXPERIMENT

The near infrared spectra of VF were recorded in two experiments. In the first experiment the bands were observed in the reaction of vanadium atoms with CF$_4$ in the presence of ~100 Torr of He in a high temperature carbon tube furnace operated at a temperature of about 2200 °C. The emission from the furnace was focused on to the entrance aperture of the 1-m Fourier transform spectrometer of the National Solar Observatory at Kitt Peak, equipped with a UV beam splitter. The 3000–9400 cm$^{-1}$ region was recorded us-

ing InSb detectors and a RG 645 filter, at a resolution of 0.05 cm$^{-1}$. Six scans were coadded in about 18 min of integration. The 9000–17 000 cm$^{-1}$ region was recorded using midrange photodiode detectors by coadding two scans in about 6 min of integration. In spite of the short integration time, the spectrum was observed with sufficient signal-to-noise ratio to be suitable for rotational analysis.

In the second experiment the bands were excited in a microwave discharge lamp with a flowing mixture of $VF_4$ vapor and He. The spectra in the 8500–12 500 cm$^{-1}$ region were recorded at a resolution of 0.02 cm$^{-1}$ by coadding 25 scans in 2.5 h of integration. This time the spectrometer was equipped with a $CaF_2$ beam splitter and the spectra were recorded using Si photodiode detectors and a RG850 filter. In this experiment the 1-0 band of VF was observed with sufficient intensity for a rotational analysis and the lines were relatively well resolved. This cooler spectrum was very helpful in the rotational analysis of the other bands recorded using the high temperature carbon tube furnace.

The new near infrared emission bands were readily attributed to VF based on their vibrational intervals and rotational line spacing. The spectral line positions were measured using a data reduction program called PC-DECOMP developed by J. Brault. The peak positions were determined by fitting a Voigt line shape function to each experimental feature. The furnace spectrum also contained the vibration-rotation bands of HCl and HF as impurities in addition to the VF bands and V atomic lines. We have used the HF[15] line positions to calibrate our spectra. The molecular lines appear with approximate widths of 0.075 cm$^{-1}$ (furnace) and 0.040 cm$^{-1}$ (microwave discharge) and a maximum signal-to-noise ratio of about 13:1. The line positions are expected to be accurate to ±0.007 cm$^{-1}$. However, there is considerable overlapping and blending due to the rotational structure of different subbands in the same region, so the uncertainty is somewhat higher for blended and weaker lines.

## RESULTS AND DISCUSSION

A number of new VF bands were observed in the 9000–15 000 cm$^{-1}$ interval in the furnace spectrum, of which the bands observed in the 9000–12 000 cm$^{-1}$ region were the most intense. Prominent bands with $R$ heads near 9156.8, 9816.4, 10 481.4, 11 035.8, and 11 587.2 cm$^{-1}$ can readily be identified as the 0-2, 0-1, 0-0, 1-0, and 2-0 bands of a new electronic transition on the basis of their intensity and vibrational spacing. The bands present in the 12 000–15 000 cm$^{-1}$ region are very weak and their heads could not be measured precisely. Much improved spectra of this region are necessary before any interpretation of the visible bands can be offered. A compressed portion of the near infrared transition of VF is presented in Fig. 1. As seen in Fig. 1, each band appears to be very complex because of the overlapping of the rotational structure of different subbands of a high multiplicity transition.

In our previous studies of transition metal halides we have noted a similarity between the electronic energy levels of transition metal halides and the corresponding hydrides. For example, the structure of TiF[16] and TiCl[17] closely re-
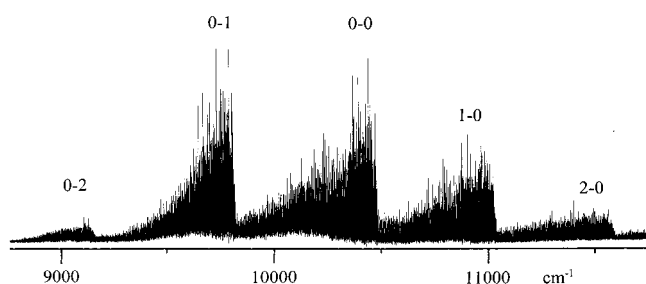


FIG. 1. A compressed portion of the $[10.5]^5\Delta - X^5\Delta$ transition of VF.

sembles that of TiH,[18] the electronic structure of HfCl[19] is similar to that of HfH[20] and the electronic structure of ScF[21,22] is very similar to that of ScH.[23,24] This suggests that the electronic structure of VF is likely to be similar to that of VH and VCl. In a recent theoretical predictions for VH, Bruna[14] has predicted a $^5\Delta$ ground state and a strong $^5\Delta - X^5\Delta$ transition near 10 650 cm$^{-1}$. Indeed, we have observed a strong (but perturbed) transition ($^5\Delta - ^5\Delta$?) of VH[25] near 7400 cm$^{-1}$. For VCl, we have recently observed a near infrared electronic transition near 7004 cm$^{-1}$ which has been assigned as the $[7.0]^5\Delta - X^5\Delta$ transition. The new transition of VF observed near 10 481 cm$^{-1}$ is analogous to the near infrared transitions of VCl[11] and VH.[25]

The two $^5\Delta$ states of VF are expected to display Hund's case (a) coupling leading to five subbands, $^5\Delta_{0\pm} - ^5\Delta_{0\pm}$, $^5\Delta_1 - ^5\Delta_1$, $^5\Delta_2 - ^5\Delta_2$, $^5\Delta_3 - ^5\Delta_3$, and $^5\Delta_4 - ^5\Delta_4$. Because of severe overlapping from different subbands, the rotational structure of only the $^5\Delta_1 - ^5\Delta_1$, $^5\Delta_2 - ^5\Delta_2$, $^5\Delta_3 - ^5\Delta_3$, and $^5\Delta_4 - ^5\Delta_4$ subbands could be identified in our spectra. A portion of the 0-0 band near the $R$ heads is provided in Fig. 2, in which the heads of the four assigned subbands have been marked. The $^5\Delta_{0\pm} - ^5\Delta_{0\pm}$ subband still remains to be identified. Our analysis indicates the presence of $\Lambda$-doubling in the $^5\Delta_1 - ^5\Delta_1$ and $^5\Delta_2 - ^5\Delta_2$ subbands. The subband with the largest $\Lambda$-doubling has been assigned as the $^5\Delta_1 - ^5\Delta_1$ subband. The observed pattern of rotational constants and relative magnitude of the $\Lambda$-doubling in the $^5\Delta_1 - ^5\Delta_1$ and $^5\Delta_2 - ^5\Delta_2$ subbands has been very helpful in the $\Omega$-assignment. Normally $\Lambda$-doubling is expected to be very small for $\Delta$ states and should have a $J$-dependence[26] given by $[J(J+1)]^\Omega$. However, mixing of the ground $X$ $^5\Delta$ state with the nearby $^5\Pi$ state [i.e., some Hund's case (c) behavior] would lead to observable $\Lambda$-doubling in the transition. In the
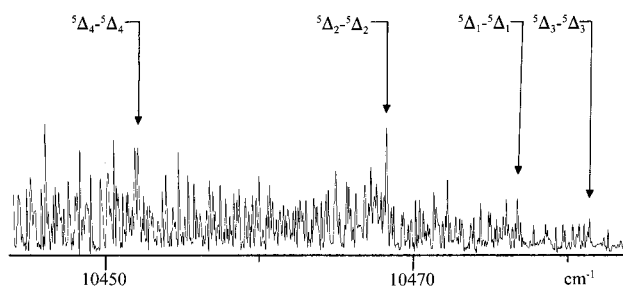


FIG. 2. A portion of the 0-0 band of the $[10.5]^5\Delta - X^5\Delta$ transition of VF with the $R$ heads marked.

TABLE I. Rotational constants (in $cm^{-1}$) for the $X^5\Delta$ and $[10.5]^5\Delta$ states of VF. (Note: Numbers in parenthesis are one standard deviation in the last digits.)

| Constants | $X\ ^5\Delta_1$ | | $X\ ^5\Delta_2$ | |
|---|---|---|---|---|
| | $v=0$ | $v=1$ | $v=0$ | $v=1$ |
| $T_{vv}$ | 0.0 | 664.8306(54) | 0.0 | 664.9096(38) |
| $B_v$ | 0.381 785(20) | 0.378 964(28) | 0.384 897(18) | 0.381 912(19) |
| $10^6\times D_v$ | 2.439(19) | 2.316(28) | 0.9039(72) | 0.8853(76) |
| $10^9\times H_v$ | 0.839(12) | 0.735(15) | 0.01872(81) | 0.01695(87) |
| $10^{13}\times L_v$ | −1.410(28) | −1.143(31) | ... | ... |
| $10^2\times q_v$ | 1.3130(43) | 1.3259(46) | 0.1074(23) | 0.1012(23) |
| $10^6\times q_{Dv}$ | −8.028(38) | −7.793(49) | 0.7178(84) | 0.745(10) |
| $10^9\times q_{Hv}$ | 2.386(23) | 2.171(29) | −0.1652(24) | −0.1716(33) |
| $10^{13}\times q_{Lv}$ | −3.259(55) | −2.717(62) | 0.1129(24) | 0.1207(36) |

| Constants | $X\ ^5\Delta_3$ | | $X\ ^5\Delta_4$ | |
|---|---|---|---|---|
| | $v=0$ | $v=1$ | $v=0$ | $v=1$ |
| $T_{vv}$ | 0.0 | 665.1019(78) | 0.0 | 665.5588(42) |
| $B_v$ | 0.385 361(33) | 0.383 182(36) | 0.387 409(17) | 0.384 190(17) |
| $10^6\times D_v$ | 5.826(41) | 6.015(44) | 0.8076(41) | 0.7781(40) |
| $10^9\times H_v$ | 1.495(23) | 1.516(24) | ... | ... |
| $10^{13}\times L_v$ | −1.822(45) | −1.801(44) | ... | ... |

| Constants | $[10.5]^5\Delta_1$ | | | $[10.5]^5\Delta_2$ | | |
|---|---|---|---|---|---|---|
| | $v=0$ | $v=1$ | $v=2$ | $v=0$ | $v=1$ | $v=2$ |
| $T_{vv}$ | 10 473.1912(34) | 11 027.1894(26) | 11 579.9959(50) | 10 464.7937(26) | 11 019.1747(24) | 11 570.7121(34) |
| $B_v$ | 0.340 321(22) | 0.338 111(16) | 0.334 841(25) | 0.347 048(19) | 0.344 304(20) | 0.341 295(22) |
| $10^6\times D_v$ | 0.281(15) | 0.4695(56) | 0.403(21) | 0.8372(72) | 0.839(10) | 0.794(12) |
| $10^{10}\times H_v$ | −0.288(37) | ... | 1.069(62) | 0.1464(82) | 0.069(19) | 0.568(23) |
| $10^3\times q_v$ | 1.940(43) | 1.388(39) | 2.671(42) | 0.965(21) | 0.976(23) | 1.144(24) |
| $10^6\times q_{Dv}$ | −1.214(31) | −0.794(20) | −1.391(30) | −0.0654(32) | −0.1194(68) | −0.211(13) |
| $10^{10}\times q_{Hv}$ | 2.296(92) | 0.947(33) | 1.970(87) | ... | ... | 0.458(33) |
| $10^{14}\times q_{Lv}$ | −1.784(99) | ... | ... | ... | ... | ... |

| Constants | $[10.5]^5\Delta_3$ | | | $[10.5]^5\Delta_4$ | | |
|---|---|---|---|---|---|---|
| | $v=0$ | $v=1$ | $v=2$ | $v=0$ | $v=1$ | $v=2$ |
| $T_{vv}$ | 10 478.7043(55) | 11 033.2638(53) | 11 584.8900(44) | 10 447.9862(46) | 11 002.8116(41) | 11 551.3631(34) |
| $B_v$ | 0.335 514(19) | 0.332 900(22) | 0.330 332(44) | 0.355 007(22) | 0.351 849(24) | 0.349 991(20) |
| $10^6\times D_v$ | 0.3671(59) | 0.3804(84) | −0.264(63) | 1.811(17) | 1.728(20) | 1.923(10) |
| $10^{10}\times H_v$ | ... | ... | −4.00(38) | 1.420(69) | 1.373(84) | 1.471(22) |
| $10^{13}\times L_v$ | ... | ... | 1.125(78) | −0.0863(96) | −0.097(12) | ... |

$^5\Delta_1-^5\Delta_1$ subband the $\Lambda$-doubling should increase as $J(J+1)$ similar to that found in a normal $^1\Pi-^1\Pi$ transition while in the $^5\Delta_2-^5\Delta_2$ subband the $\Lambda$-doubling, if present, should increase as $[J(J+1)]^2$. The presence of large $\Lambda$-doubling in the $^5\Delta_1$ and $^5\Delta_2$ spin components is the result of strong interactions with the nearby $^5\Pi$ state.

We have analyzed the rotational structure of only the $^5\Delta_1-^5\Delta_1$, $^5\Delta_2-^5\Delta_2$, $^5\Delta_3-^5\Delta_3$, and $^5\Delta_4-^5\Delta_4$ subbands in the 0-1, 0-0, 1-0, and 2-0 bands. The rotational analysis of the 0-2 band could not be achieved because of its weak intensity (Fig. 1). The rotational structure of each subband consists of $R$ and $P$ branches (no $Q$ branch) appearing with similar intensity consistent with a $\Delta\Omega=0$ assignment. The rotational constants for the different $\Omega$ states have been obtained by fitting the observed lines to the following energy level expression:

$$F_v(J)=T_v+B_vJ(J+1)-D_v[J(J+1)]^2+H_v[J(J+1)]^3$$
$$+L_v[J(J+1)]^4\pm 1/2\{q_vJ(J+1)+q_{Dv}[J(J+1)]^2$$
$$+q_H[J(J+1)]^3+q_L[J(J+1)]^4\}. \tag{1}$$

The rotational lines were given weights according to the resolution, line intensity, and the extent of blending. The badly blended lines were heavily deweighted. The observed lines positions for the different sub-bands are available from EPAPS[27] or from the authors upon request. The molecular constants for the different bands are provided in Table I. The $e/f$ parity assignment in the $^5\Delta_1-^5\Delta_1$ and $^5\Delta_2-^5\Delta_2$ subbands was made arbitrarily to provide a positive $\Lambda$-doubling constant $q_v$ in lower state. The constants $T_v$, $B_v$, $D_v$, $H_v$, and $L_v$ are required for most of the vibrational levels of the different spin components. In addition the $\Lambda$-doubling constants $q_v$, $q_{Dv}$, $q_{Hv}$, and $q_{Lv}$ are required for the $^5\Delta_1$ and $^5\Delta_2$ spin components to minimize the standard deviation of the fits. The determination of the higher order constants is a reflection of the strong interaction with nearby states.

Although the visible spectrum of VF has been known for decades, the identity of the ground state has been an open question. The present work provides the first high resolution data for VF and sheds some light on the nature of the ground electronic state. The observation of several subbands for

each vibrational band is consistent with the assignment of the high multiplicity transition. Our assignment of the $^5\Delta$ ground state is consistent with available results for VH[14] and our recent observation of an infrared electronic transition of VCl.[11] In a more recent study of VCl, an *ab initio* calculation has been performed on the low-lying electronic states, and the analysis of the $[7.0]^5\Delta - X^5\Delta$ transition has been extended by analyzing many more bands.[28] It was also possible to identify an additional subband in spite of severe blending.[28] This study supports our $^5\Delta$ assignment for the ground state of VCl[11] and suggests that VF should also have a $^5\Delta$ ground state. Note, however, that the previously suggested[10] $^5\Pi$ ground state assignment for VF cannot be completely ruled out.

An irregular variation in the rotational and distortion constants of the different spin components of both the ground and excited states is the result of strong interaction with close-lying states. The large $\Lambda$-doubling in the $^5\Delta_1$ and $^5\Delta_2$ spin components is most probably the result of strong interactions with close-lying $^5\Pi$ states. The effects of these interactions are also apparent in the observed local and global perturbations. In the 0-0 and 1-0 bands of the $^5\Delta_1-^5\Delta_1$ subband, the lines with $e$-parity are affected for $J''>45$. The high $J$ $e$-parity lines could not be identified with certainty while the $f$-parity levels are unaffected. The $^5\Delta_2-^5\Delta_2$ subband is free from local perturbations. In the $^5\Delta_3-^5\Delta_3$ subband the observed minus calculated difference in the line positions of the 0-1 and 0-0 bands suggests that $v''=0$ and 1 levels are affected for $J''\gtrsim 50$. Similarly, the negative value of the distortion constant of the $v'=2$ vibrational level of the $^5\Delta_3$ spin component of the excited state is the result of interactions in the excited state. The $^5\Delta_4-^5\Delta_4$ subband is also free from local perturbations, although in the 0-0 band of the $^5\Delta_4-^5\Delta_4$ subband the lines seem to split into two components after approximately $J=52$. The split lines in the $\Omega=4$ subband were not included in the fit because of their poor intensity.

We have used the observed band head positions to calculate approximate vibrational constants for VF. The location of the highest wave number $R$ head of the 0-2, 0-1, 0-0, 1-0, and 2-0 bands near 9156.8, 9816.4, 10 481.4, 11 035.8, and 11 587.2 cm$^{-1}$, respectively, provides the following approximate vibrational constants for the ground and excited states of VF: $\omega_e''=670.4$ cm$^{-1}$, $\omega_e x_e''=2.7$ cm$^{-1}$, $\omega_e'=557.4$ cm$^{-1}$, and $\omega_e x_e'=1.5$ cm$^{-1}$. The ground state vibrational constants from this transition are, however, considerably different from those reported by Jones and Krishnamurthy[10] from the low resolution emission spectrum of the visible bands.

The spectroscopic constants for the different vibrational levels of the ground and excited states provided in Table I have been used to determine approximate Hund's case (a) constants. Because the constants of the different spin components of the ground and excited states vary in an irregular manner, a simple average of these constants has been taken to obtain approximate Hund's case (a) constants. The average of the ground state vibrational intervals from Table I provides $\Delta G''(1/2)=665.10$ cm$^{-1}$. The average of the $B$ values listed in Table I provides $B_0''$

$=0.3849$ cm$^{-1}$, and $B_1''=0.3821$ cm$^{-1}$ yielding $B_e''=0.3863$ cm$^{-1}$, $\alpha_e''=0.0028$ cm$^{-1}$, and $r_e''=1.7758$ Å. A calculation for the excited state results in the values of $\Delta G(1/2)=554.44$ cm$^{-1}$, $\Delta G(3/2)=551.13$ cm$^{-1}$, $B_0=0.3445$ cm$^{-1}$, $B_1=0.3418$ cm$^{-1}$, and $B_2=0.3393$ cm$^{-1}$. The excited state equilibrium constants using these values are $\omega_e'=557.75$ cm$^{-1}$, $\omega_e x_e'=1.66$ cm$^{-1}$, $B_e'=0.3458$ cm$^{-1}$, $\alpha_e'=0.0026$ cm$^{-1}$, and $r_e'=1.8769$ Å.

The lowest energy term of the V$^+$ atom is $a$ $^5D$, which arises from the $3d^4$ configuration.[29] The $a$ $^5D$ term is split by the ligand field of F$^-$ and correlates to the $^5\Delta$, $^5\Pi$, and $^5\Sigma^-$ molecular states in order of increasing energy. The first excited term in V$^+$ is $a$ $^5F$ at $\sim 3000$ cm$^{-1}$ arising from the $3d^34s^1$ configuration.[29] The molecular states correlating to the $a$ $^5F$ term are $^5\Phi$, $^5\Delta$, $^5\Pi$, and $^5\Sigma^+$ states which form a cluster of states in the 7000–10 000 cm$^{-1}$ range as calculated for VH.[14] Our near infrared transition of VF is, therefore, between the two $^5\Delta$ states derived from the $a$ $^5D$ and $a$ $^5F$ terms of V$^+$. A $^5\Delta$ ground state for VF has been predicted by Averyanov and Khait[12] as does a high level calculation by Bruna *et al.* on VH,[14] although the *ab initio* calculation of Harrison[13] on VF did not lead to a definite conclusion about the identity of the ground state (either $^5\Delta$ or $^5\Pi$).

Some useful conclusions can be drawn from the spectroscopic constants listed in Table I. The significant $\Lambda$-doubling in the $^5\Delta_1$ and $^5\Delta_2$ spin components of both states indicates that they are strongly mixed with the spin components of nearby states. Averyanov and Khait[12] predict a $^5\Pi$ state at 1700 cm$^{-1}$ above the $X$ $^5\Delta$ state for VF, while for VH a $^5\Pi$ state is predicted at about 800 cm$^{-1}$ above the ground state. This is also consistent with the Harrison's theoretical predictions[13] for VF which suggests very close-lying $^5\Delta$ and $^5\Pi$ states. The large $\Lambda$-doubling in the ground state is therefore due to strong interaction with this $^5\Pi$ state. Similar interactions are also possible for the excited $^5\Delta$ state, although an *ab initio* calculation predicting all the low-lying states of VF is still lacking.

## CONCLUSION

We have observed the thermal emission spectrum of VF in the 3400–17 000 cm$^{-1}$ region using a Fourier transform spectrometer. Five groups of bands with $R$ heads (highest wave number subband) near 9156.8, 9816.4, 10 481.4, 11 035.8, and 11 587.2 cm$^{-1}$ have been assigned as the 0-2, 0-1, 0-0, 1-0, and 2-0 bands of the $[10.5]^5\Delta - X^5\Delta$ transition. The 1-0 band of this transition has also been observed using a microwave discharge lamp. A rotational analysis of the $^5\Delta_1-^5\Delta_1$, $^5\Delta_2-^5\Delta_2$, $^5\Delta_3-^5\Delta_3$, and $^5\Delta_4-^5\Delta_4$, subbands of the 0-1, 0-0, 1-0, and 2-0 bands has been obtained and molecular constants have been extracted. The large $\Lambda$-doubling observed in the $^5\Delta_1$ and $^5\Delta_2$ spin components is probably a reflection of a strong interaction with nearby $^5\Pi$ states. The lower $^5\Delta$ state is most likely the ground state of VF as predicted,[12,13] and observed for VCl[11,28] but we do not have any direct evidence to prove this. Further experimental and theoretical work on VF will be necessary to confirm our assignments.

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