Fourier transform infrared emission spectroscopy of VCl

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The high resolution spectrum of VCl has been observed in emission in the 3000–9400 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 and a trace of BCl_3 and the spectra were recorded at a resolution of 0.05 cm^{-1}. The new bands observed in the 6000–8000 cm^{-1} interval have been attributed to VCl. The bands having R heads near 6176, 6589, 7004, 7358, and 7710 cm^{-1} have been assigned as the 0–2, 0–1, 0–0, 1–0, and 2–0 bands, respectively, of the $[7.0]^5\Delta - X\,^5\Delta$ electronic transition. A rotational analysis of the $^5\Delta_1 - ^5\Delta_1$, $^5\Delta_2 - ^5\Delta_2$, and $^5\Delta_3 - ^5\Delta_3$ subbands of the 0–1 and 0–0 vibrational bands has been obtained and molecular constants have been extracted. The remaining two of the five subbands could not be analyzed because of severe overlapping from neighboring subbands. The principal molecular constants for the $X\,^5\Delta$ state obtained from the present analysis are: $\Delta G(1/2) = 415.26(113)$ cm^{-1}, $B_e = 0.165\,885(250)$ cm^{-1}, $\alpha_e = 0.000\,586(84)$ cm^{-1}, and $r_e = 2.213\,79(170)$ Å. Our work represents the first observation of this near infrared electronic transition of VCl. © *2001 American Institute of Physics.*
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INTRODUCTION

The study of transition metal-containing molecules has attracted considerable recent attention because of their importance in astrophysics[1,2] and chemistry.[3,4] These molecules are also of theoretical interest.[5–10] While most of the diatomic transition metal oxides[11] and hydrides[12] have been relatively well characterized and many of the nitrides have recently been investigated,[13,14] only a few transition metal halides have been studied so far. In the group 5 transition metal family only limited low resolution data on VF,[15] VCl,[16] and TaCl[17] are available in literature. Some visible bands of VF have been observed by Jones and Krishnamurty[15] at low resolution and electronic assignments of $^5\Sigma - ^5\Pi$ or $^5\Delta - ^5\Pi$ have been proposed for these bands. The emission spectrum of VCl has previously been observed by Iacocca *et al.*[16] in the visible region. This spectrum consisted of only the $\Delta v = 0$ sequence bands and thus no vibrational constants were obtained and no electronic assignments were proposed. For TaCl, only a brief mention of a few visible bands was made in a thesis[17] where TaN bands were produced from a microwave excitation of a $TaCl_4$ vapor, N_2, and He mixture. Again no attempts were made to obtain the vibrational or electronic assignments for the TaCl bands.

There is an *ab initio* calculation for the quintet states of VF which proposes a $^5\Delta$ ground state.[18] Some *ab initio* calculations have been performed for VH by Bruna[19] and VF by Harrison[20] and the spectroscopic properties for the low-lying

electronic states have been predicted. For VF the ground state was predicted to be either $^5\Delta$ or $^5\Pi$ but no definite conclusion was drawn about which state is lower in energy.[20] On the other hand a $^5\Delta$ ground state was predicted for VH[19] on the basis of a high quality *ab initio* calculation.[19] In general, transition metal halides and hydrides have very similar structure so we expect that the ground states of VF and VCl are most probably $^5\Delta$ states.

In the present work we report on the observation of a new electronic transition of VCl in the 6000–8000 cm^{-1} region. We have assigned this transition as $[7.0]^5\Delta - X\,^5\Delta$. A rotational analysis of the 0–0 and 0–1 bands of the $^5\Delta_1 - ^5\Delta_1$, $^5\Delta_2 - ^5\Delta_2$, and $^5\Delta_3 - ^5\Delta_3$ subbands has been obtained. Although the rotational analysis of the remaining two subbands ($^5\Delta_{0\pm} - ^5\Delta_{0\pm}$, $^5\Delta_4 - ^5\Delta_4$) could not be obtained because of overlapping from the other subbands, the present assignment is consistent with the expectations based on the *ab initio* calculations of Bruna for VH.[19]

EXPERIMENT

The initial experiment was intended to observe VH bands near 1 μm using the high temperature reaction of V and H_2. We have previously observed VH in a hollow cathode discharge[21] but the bands remain unanalyzed mainly because of strong perturbations. In the furnace we did not observe the VH bands and, therefore, decided to search for bands of VF and VCl instead. The near infrared bands of VCl were observed from the reaction of V atoms with BCl_3 in a high temperature carbon tube furnace operated at a tem-
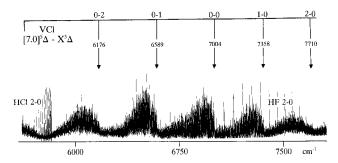
FIG. 1. A compressed portion of the $[7.0]^5\Delta - X^5\Delta$ transition of VC1.

perature 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 and the spectra were recorded using an InSb detector and a RG 645 filter at a resolution of 0.05 cm^{-1}. The spectrum was recorded with only a single scan in about 3 min. In spite of this short integration time, the spectrum was observed with sufficient signal-to-noise ratio for high resolution analysis.

A number of new bands observed in the 6000–8000 cm^{-1} region were readily attributed to VCl 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 Brault. The peak positions were determined by fitting a Voigt line shape function to each experimental feature. The observed spectra also contained the vibration–rotation bands of HCl and HF as impurities in addition to the VCl bands and V atomic lines. We have used the HF[22] line positions to calibrate our spectrum. The molecular lines appear with a width of 0.070 cm^{-1} and maximum signal-to noise ratio of about 8:1; the line wave numbers 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 compressed portion of the observed spectrum is presented in Fig. 1. The bandheads observed near 6176, 6589, 7004, 7358, and 7710 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. This transition has been assigned as a $^5\Delta - ^5\Delta$ transition. As seen in Fig. 1, the spectrum of each band is very complex because of the crowded overlapping of the rotational structure of different subbands. In fact, the overlapping is so severe that the rotational structure of all five subbands could not be unambiguously identified. The recent theoretical predictions for VH by Bruna[19] were very helpful in assigning our electronic transition. The ground state of VH is predicted to be a $^5\Delta$ state and a strong $^5\Delta - X^5\Delta$ transition has been predicted near 10 650 cm^{-1}. Indeed, we find a strong complex transition ($^5\Delta - ^5\Delta$?) of VH[20] near 7400 cm^{-1}. In our previous studies of transition metal halides we have noted the similarity between the electronic energy levels of transition metal halides and the correspond-

ing hydrides. For example, the structure of TiF[23] and TiCl[24] closely resembles that of TiH[25] and the electronic structure of HfCl[9] is similar to that of HfH.[26] The VF and VCl molecules probably have a $^5\Delta$ ground state like VH[19] and we assign the observed VCl bands to a $^5\Delta - ^5\Delta$ transition. The 0–0 band of this transition is located near 7004 cm^{-1}, and we have, therefore, decided to label this transition as $[7.0]^5\Delta - X^5\Delta$.

The $^5\Delta$ states 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 $^5\Delta_4 - ^5\Delta_4$. Normally Λ doubling is expected to be small for Δ states and have J dependence[27] 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] could lead to observable Λ doubling (or more correctly Ω doubling). The effects of Λ doubling should then be apparent in the $^5\Delta_1 - ^5\Delta_1$ and $^5\Delta_2 - ^5\Delta_2$ subbands. In the $^5\Delta_1 - ^5\Delta_1$ subband the Λ doubling should increase as J (JH) J, similar to that found in a normal $^1\Pi - ^1\Pi$ transition. The observed rotational structure of this subband is consistent with this expectation. In the $^5\Delta_2 - ^5\Delta_2$ subband the Λ doubling, if present, should increase as $[J(J+1)]^2$ similar to a $^3\Pi_2 - ^3\Pi_2$ transition. The observed rotational structure of this subband is also consistent with this expectation and a very small doubling is seen at very high J values ($J > 63$).

The observed pattern of Λ doubling in these two subbands has been very helpful in the Ω assignment of different subbands. Surprisingly some small Ω doubling has also been observed in the $^5\Delta_3 - ^5\Delta_3$ subband for $J > 82$. This observation is consistent with some Hund's case (c) behavior in the lower state as discussed in the following. We have analyzed the rotational structure of only the $^5\Delta_1 - ^5\Delta_1$, $^5\Delta_2 - ^5\Delta_2$, and $^5\Delta_3 - ^5\Delta_3$ subbands in the 0–0 and 0–1 bands. The rotational analysis of 0–2, 1–0, and 2–0 bands could not be achieved because they were weak. The rotational structure of each subband consists of R and P branches (no Q branch) appearing with similar intensity indicating a $\Delta\Omega = 0$ assignment. The rotational constants for the different Ω states have been obtained by fitting the observed lines to the following energy level expression:

$$F_v(J) = T_v + B_v J(J+1) - D_v [J(J+1)]^2$$
$$+ H_v [J(J+1)]^3 \pm 1/2\{q_v J(J+1)$$
$$+ q_{D_v}[J(J+1)]^2 + q_{H_v}[J(J+1)]^3\}. \quad (1)$$

The rotational lines were weighted according to resolution and the extent of blending. The badly blended lines were heavily deweighted. The observed lines positions for the different subbands are available from EPAPS[28] 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 $^5\Delta_1 - ^5\Delta_1$ subband was made arbitrarily to provide a positive Λ-doubling constant q_v in the $X^5\Delta_1$ spin component. The parity assignments in the $^5\Delta_2 - ^5\Delta_2$ and $^5\Delta_3 - ^5\Delta_3$ subbands were also chosen arbitrarily. The higher order Ω-doubling constant p_{D_v} was also determined for the $v = 0$ and 1 vibrational levels of the $X^5\Delta_1$ spin component. Likewise p_{D_v} and p_{H_v} were determined for the $v = 0$ vibrational

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TABLE I. Spectroscopic constants for the $[7.0]^5\Delta - X\,^5\Delta$ transition of VCl. a, b, c refer to the undetermined term values of the $v=0$ vibrational levels of $X\,^5\Delta_1$, $X\,^5\Delta_2$, and $X\,^5\Delta_3$ spin components, respectively.

State	v	T_v	B_v	$10^7 \times D_v$	$10^{12} \times H_v$	$10^3 \times q_v$	$10^8 \times q_{D_v}$	$10^{14} \times q_{H_v}$
$[7.0]^5\Delta_3$	0	c+6951.4112(14)	0.156 212 6(63)	1.7274(41)	1.4043(82)	...	...	...
$[7.0]^5\Delta_2$	0	b+6985.9662(17)	0.154 722 8(84)	1.2276(78)	...	...	...	...
$[7.0]^5\Delta_1$	0	a+7001.9264(21)	0.153 384(11)	1.049(13)	...	...	...	...
	1	c+413.6719(21)	0.165 385 6(63)	1.1682(40)	...	...	...	...
$X\,^5\Delta_3$	0	c	0.165 928 2(62)	1.1637(37)	...	...	...	6.18(11)
	1	b+416.2044(25)	0.165 098 6(88)	0.9989(99)	−0.566(31)	...	...	...
$X\,^5\Delta_2$	0	b	0.165 610 0(86)	0.9545(87)	−1.568(26)	...	−0.1755(34)	...
	1	a+415.9116(29)	0.164 532(11)	1.211(13)	...	1.0642(12)	−6.979(25)	...
$X\,^5\Delta_1$	0	a	0.165 236(18)	1.154(13)	...	1.1133(14)	−7.282(30)	...

level of the $^5\Delta_2$ and $^5\Delta_3$ spin components, respectively, of the ground state. Note that no Λ-doubling constants could be determined for the excited state so they were set to zero.

Although the visible spectrum of VCl has been known for decades, the identity of the ground state is still an open question. The observation of several subbands in the near infrared bands is consistent with the assignment of high multiplicity states. The previously suggested $^5\Pi$ ground state assignment for VF (or for VCl) is not consistent with the $^5\Delta$ ground state of VH,[19] although it may not be completely ruled out. The observed bandhead positions have been used to calculate the approximate vibrational constants for the ground and excited states. Using the highest wave number bandhead positions, the following approximate vibrational constants have been determined for the ground and excited states: $\omega_e''=417\ \text{cm}^{-1}$, $\omega_e x_e''=1\ \text{cm}^{-1}$, $\omega_e'=356\ \text{cm}^{-1}$, and $\omega_e x_e'=1\ \text{cm}^{-1}$. The rotational constants obtained for the $v=0$ and 1 vibrational levels can be used to determine the equilibrium rotational constants for the $^5\Delta_1$, $^5\Delta_2$, and $^5\Delta_3$ spin components of the ground state. The values of $B_e=0.165\,588(21)\ \text{cm}^{-1}$, $\alpha_e=0.000\,704(21)\ \text{cm}^{-1}$ for the $X\,^5\Delta_1$, $B_e=0.165\,866(11)\ \text{cm}^{-1}$, $\alpha_e=0.000\,511(12)\ \text{cm}^{-1}$ for the $X\,^5\Delta_2$ and $B_e=0.166\,199\,5(76)\ \text{cm}^{-1}$, $\alpha_e=0.000\,542\,6(88)\ \text{cm}^{-1}$ for the $X\,^5\Delta_3$ spin component have been obtained. The observed term values for the three spin components provide the $\Delta G(1/2)$ vibrational intervals of 415.9116(29) cm^{-1}, 416.2044(25) cm^{-1}, and 413.6719(21) cm^{-1} for the $X\,^5\Delta_1$, $X\,^5\Delta_2$, and $X\,^5\Delta_3$ spin components, respectively. The irregular variation in the vibrational intervals can be attributed to the interactions with the slightly higher-lying $^5\Pi$ state. The three subbands analyzed in this work involve the three middle spin components of the ground and excited states, the average of the effective $\Delta G(1/2)$, B_e and α_e values need to be computed to derive the Hund's case (a) constants for the ground and excited states. This calculation provides $\Delta G(1/2)=415.26(113)\ \text{cm}^{-1}$, $B_e=0.165\,885(250)\ \text{cm}^{-1}$, $\alpha_e=0.000\,856(84)\ \text{cm}^{-1}$ for the ground $X\,^5\Delta$ state. The equilibrium rotational constant results in the equilibrium ground state bond length of $r_e''=2.213\,79(170)$ Å. A value of $r_0'=2.291\,88(110)$ Å has been obtained for the excited state using the average value of $B_0'=0.154\,773(150)\ \text{cm}^{-1}$.

The previous *ab initio* calculation of Harrison[20] on VF did not lead to a definite conclusion about the identity of the ground state (either $^5\Delta$ or $^5\Pi$). Averyanov and Khait,[18] however, predict a $^5\Delta$ ground state as does a high level calculation on VH.[19] Some valuable conclusions can be drawn from the spectroscopic constants listed in Table I. As seen in Table I, Λ doubling of significant magnitude has been obtained in the $X\,^5\Delta_1$ spin component while no Λ doubling was obtained in the $^5\Delta_1$ spin component of the excited state. This indicates that the excited $[7.0]^5\Delta$ state is a relatively isolated state whereas the $X\,^5\Delta_1$ spin component is mixed with a nearby state. This is consistent with Harrison's theoretical predictions[20] for VF. Averyanov and Khait[18] predict that the $^5\Pi$ state is 1700 cm^{-1} above the $X\,^5\Delta$ state for VF, while the corresponding value for VH is about 800 cm^{-1}.

As for other transition metal halides, useful information about electronic structure can be derived from the atomic energy levels[29] of V$^+$. The lowest term of V$^+$ is $a\,^5D$ derived from the $3d^4$ configuration. The ligand field of Cl$^-$ will split this term into $^5\Delta$, $^5\Pi$, $^5\Sigma^-$ states in order of increasing energy. This prediction is borne out by the calculations on VF[18,20] and VH.[19] The next term in V$^+$ is $a\,^5F$ at about 3000 cm^{-1} arising from the $3d^3 4s^1$ configuration. This term correlates to the $^5\Phi$, $^5\Delta$, $^5\Pi$, $^5\Sigma^+$ cluster of states found in the 7000–10 000 cm^{-1} range for VH. Our $^5\Delta - X\,^5\Delta$ transition is thus between the two $^5\Delta$ states derived from the lowest energy $a\,^5D$ and $a\,^5F$ terms of V$^+$.

CONCLUSION

We have observed the thermal emission spectrum of VCl in the 3000–9400 cm^{-1} region using a Fourier transform spectrometer. Five groups of bands with R heads (for the highest wave number subbands) near 6176, 6589, 7004, 7358, and 7710 cm^{-1} have been assigned as the 0–2, 0–1, 0–0, 1–0, and 2–0 bands of the $[7.0]^5\Delta - X\,^5\Delta$ transition. A rotational analysis of the $^5\Delta_1 - ^5\Delta_1$, $^5\Delta_2 - ^5\Delta_2$, and $^5\Delta_3 - ^5\Delta_3$ subbands of the 0–1 and 0–0 bands has been obtained and molecular constants have been extracted. Most likely the lower $X\,^5\Delta$ state is the ground state but we do not have any direct evidence to prove this. Further experimental and theoretical work on VCl will be necessary to test our proposed assignment, and this work is under way.

ACKNOWLEDGMENTS

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[28] See EPAPS Document No. EJCPSA6-114-015111 for line positions for the near infared transition of VCl. This document may be retrieved via the EPAPS homepage (http://www.AIP.org/pubservs/epaps.html) or from ftp.AIP.org in the directory/epaps/. See the EPAPS homepage for more information.

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