EMISSION SPECTROSCOPY AND *AB INITIO* CALCULATIONS ON VCl AND VF

R. S. RAM, *Department of Chemistry, University of Arizona, Tucson, AZ 85721*; J. LI'EVIN, *Université Libre de Bruxelles, Laboratoire de Chimie Physique Moléculaire, CP 160/09, Av. F. D. Roosevelt 50, Bruxelles, Belgium*; P. F. BERNATH, *Department of Chemistry, University of Waterloo, Ont., Canada N2L 3G1*; S. P. DAVIS, *Department of Physics, University of California, Berkeley, CA 94720.*

The emission spectra of VCl and VF have been investigated in the 3400-17000 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 vapors with BCl_3 and CF_4, respectively. The VF bands were also observed in a microwave discharge through a flowing mixture of VF_4 vapor and helium. The VCl bands with high wavenumber R heads near 6176.0, 6589.6, 7004.1, 7358.2 and 7710.0 cm^{-1} have been assigned as the 0-2, 0-1, 0-0, 1-0 and 2-0 bands of the $[7.0]^5\Delta - X^5\Delta$ electronic transition while the VF bands with R heads near 9156.8, 9816.4, 10481.4, 11035.8 and 11587.2 cm^{-1} have been assigned as the 0-2, 0-1, 0-0, 1-0 and 2-0 bands, respectively, of the $[10.5]^5\Delta - X^5\Delta$ transition. 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 several bands of VCl and VF has been carried out and spectroscopic parameters have been obtained. Equilibrium constants of ω_e=417.37 cm^{-1}, $\omega_e x_e$=3.5 cm^{-1}, B_e=0.1658 cm^{-1}, α_e=0.0006 cm^{-1} and r_e=2.2137 Å have been obtained for the ground state of VCl, while equilibrium constants of $\Delta G(½)$=665.10 cm^{-1}, B_e=0.3863 cm^{-1}, α_e=0.0028 cm^{-1} and r_e= 1.7758 Å have been determined for the ground state of VF. The spectroscopic properties of the low-lying electronic states of VCl have also been predicted by *ab initio* calculations. Our electronic assignments are supported by the results of our *ab initio* calculations.