

Force Constants, Mean Amplitudes of Vibration, Shrinkage Effects, Coriolis Constants, and Thermodynamic Functions of Vanadium Pentafluoride

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The following quantities have been calculated from spectroscopic data for vanadium pentafluoride: Force constants, mean amplitudes of vibration, Bastiansen—Morino shrinkage effects, Coriolis coupling constants, and thermodynamic properties. The calculations are based on a recent assignment of vibrational frequencies (from Claassen and Seelig), which supports the assumption of a trigonal bipyramidal structure. As the equilibrium distance we applied the value of 1.71 Å for both equatorial and axial V—F, as was recently obtained from electron diffraction (Romanov and Spiridonov). The calculated mean amplitudes for V—F equatorial and axial at 298°K amount to 0.0405 and 0.0431 Å, respectively.

Recently Brunvoll¹ has calculated the mean amplitudes of vibration for several bipyramidal XY_5 and XY_3Z_2 molecules with D_{3h} symmetry. These calculations also include SbF_5 . We wish therefore to mention that according to an investigation of Müller *et al.*² this molecule is polymeric at room temperature, and the earlier assignments of vibrational frequencies for SbF_5 are not correct. As, in the meantime, Claassen *et al.*³ have given the complete vibrational spectrum of VF_5 , and Romanov *et al.*⁴ have made an electron diffraction study of this compound, we have calculated some molecular constants of VF_5 from spectroscopic data.

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The correct G matrix for a molecule of the considered type, but with equal bond lengths, has been reported by Müller *et al.*⁵ The symmetry force constants of the species $A_2'' + E'$ have been calculated with the method of Fadini⁶ and are summarized in Table 1. The force constants for the one-

Table 1. Symmetry force constants of VF_5 .

	mdyne/Å		mdyne/Å
$F_{11}(A_2'')$	3.88	$F_{11}(E')$	4.60
$F_{12}(A_2'')$	0.11	$F_{12}(E')$	-0.01
$F_{22}(A_2'')$	0.38	$F_{13}(E')$	0.02
		$F_{22}(E')$	0.21
		$F_{23}(E')$	0.02
		$F_{33}(E')$	0.23

dimensional species $A_1' + E''$ can be obtained directly from the frequencies. The symmetry coordinates are the same as used in Ref. 5.

The mean amplitudes of vibration^{7,8} (u) and the Bastiansen—Morino shrinkage effects^{8,9} are given in Table 2. In the computation of these quantities

Table 2. Mean amplitudes of vibration (u) and Bastiansen—Morino shrinkage effects of VF_5 in Å.

Distance	u		Shrinkage	
	$T = 0$	298°K	$T = 0$	298°K
V—F (eq.)	0.0395	0.0405		
V—F (ax.)	0.0415	0.0431		
F...F (eq./eq.)	0.0620	0.0748	0.0019	0.0029
F...F (ax./ax.)	0.0540	0.0570	0.0037	0.0077
F...F (eq./ax.)	0.0693	0.0882	0.0009	0.0014

the force constants of Table 1 were used, along with the bond length of V—F = 1.71 Å given by Romanov *et al.*⁴ Although these authors have published the radial-distribution function they have not given the u values. The present values of mean amplitudes (u) should replace those of the previously reported calculations.⁶

We have also calculated the first-order Coriolis coupling constants¹⁰ (ζ). In this case one has nonvanishing first-order ζ values of the type $E' \times E'$ and $E'' \times E''$. The diagonal elements of the corresponding ζ matrix are important in the studies of infrared band contours of symmetrical top molecules. These elements are found according to our calculations for VF_5 in Table 3.

Table 3. Coriolis coupling constants of VF_5 .

		ν (cm^{-1})
$\zeta_1(E' \times E')$	0.45	810
$\zeta_2(E' \times E')$	-0.41	282
$\zeta_3(E' \times E')$	0.95	200
$\zeta_1(E'' \times E'')$	0.43	350

Because of the publication⁴ of an experimental bond length for VF_5 we have repeated the calculations of thermodynamic functions for this molecule, using the model of rigid rotator and harmonic oscillator. The obtained values are given in Table 4 and agree fairly well with those of Ref. 5, which are based on an estimated bond length.

Table 4. Specific heat, enthalpy, free energy and entropy for the ideal gaseous state of 1 atm pressure of VF_5 in cal degree⁻¹ mol⁻¹.

T °K	C_p°	$(H^\circ - H_0^\circ)/T$	$-(F^\circ - H_0^\circ)/T$	S°
200	19.25	12.59	56.72	69.30
273.16	22.65	14.85	60.98	75.83
298.16	23.56	15.54	62.31	77.86
300	23.62	15.59	62.41	78.00
400	26.30	17.96	67.24	85.20
500	27.93	19.81	71.45	91.26
600	28.96	21.25	75.19	96.45
700	29.64	22.41	78.56	100.97
800	30.11	23.34	81.62	104.96
900	30.44	24.11	84.41	108.52
1000	30.69	24.76	86.99	111.74
1100	30.87	25.31	89.37	114.68
1200	31.01	25.78	91.59	117.37
1300	31.13	26.18	93.67	119.86
1400	31.22	26.54	95.63	122.17
1500	31.29	26.85	97.47	124.32
1600	31.35	27.13	99.21	126.34
1700	31.40	27.38	100.86	128.25
1800	31.44	27.61	102.44	130.04
1900	31.48	27.81	103.93	131.74
2000	31.51	27.99	105.37	133.36

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