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VIBRATIONAL SPECTRA OF VANADIUM CHLORIDE AND ITS NORMAL COORDINATE ANALYSIS

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This paper presents the Fourier far infrared and laser Raman spectra of vanadium chloride from 600 to 70cm^{-1} and 50–2000cm^{-1} respectively. The spectra have been analysed in terms of fundamentals, combinations and overtones assuming C_{3v} point group. The fundamental frequencies of vanadium chloride are :

(A_1) = 392 and 160cm^{-1},

(E) = 473 and 205cm^{-1}

Further, a normal co-ordinate analysis has been carried out following Wilson's **F-G** matrix method and a set of molecular constants have been evaluated. The thermodynamic properties are presented over the temperature range 298.16 **K** to 1000 K.

Key Words : Infrared and Laser Raman Spectra; Vanadium Chloride; Force Field; Molecular Constants

INTRODUCTION

SPECTROSCOPIC studies of pyramidal molecules have evoked interest of several workers in the recent past.[1–5] In the course of our investigation on the study of molecular constants of pyramidal molecules our attention has been turned to vanadium chloride. Although the material is known for a long time, a complete spectral data have not been reported for this compound. In the present paper, the Fourier far infrared and laser Raman spectra of vanadium chloride have been reported. The vibrational frequencies of this molecule have been assigned on the basis of pyramidal C_{3v} symmetry. Its spectrum consists of four normal vibrations; two belonging to A_1 type symmetry species and two to doubly degenerate E-type symmetry species.

EXPERIMENTAL

Vanadium chloride of high grade purity was procured from M/s Fluka Ag., Switzerland. The Fourier transform far IR spectrum has been recorded in the

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region 600 to 70cm^{-1} on Polytech FIR-30 spectrophotometer. The Laser Raman spectrum has also been recorded on cary model 82 spectrophotometer equipped with argon laser of power 4000mw in the region 50 to 4000cm^{-1}. Results of far infrared and laser Raman studies of this molecule is summarised in Table I. The frequencies for all sharp bands are expected to be accurate to $\pm$ 1cm^{-1}.

TABLE I

Infrared and laser Raman frequencies (cm^{-1}) of vanadium-trichloride

Infrared		Assignment	Raman	
Frequency	Intensity+		Intensity+	Frequency
95	*W*	$2\nu_4 - 2\nu_2$		
160	*S*	ν_2(Cl–V–Cl symmetric bending)	*S*	162
205	*W*	ν_4(Cl–V–Cl asymmetric bending)	*W*	210
250	*M*	$2\nu_4 - \nu_2$		
320	*VS*	$2\nu_2$		
392	*M*	ν_1(V–Cl symmetric stretch)	*S*	381
416	*M*	$2\nu_4$		
473	*M*	ν_3(V–Cl asymmetric stretch)	*M*	475
528	*W*	$2\nu_3 - 2\nu_4$		

+*VS*—very strong; *S*—strong; *M*—Medium; *W*—Weak.

RESULTS AND DISCUSSION

The present study of infrared spectrum of vanadium chloride, combined with the laser Raman studies gives a clear pictute of the structure of the compound.

Four fundamental absorption bands have been observed at 473, 392, 205 and 160cm^{-1}. The vibrational representation of a XY_3 planar (D_{3h}) molecule is represented as $\Gamma = A_1 + A_2'' + 2E'$, whereas that of a XY_3 pyramidal (C_{3v}) molecule is $\Gamma = 2A_1 + 2E$. Accordingly, in a planar molecule, only three frequencies (A_2'' and $2E'$) are infrared active, while in a pyramidal system all the four frequencies ($2A_1$ and $2E$) should be active in the infrared. In both the systems, the ν_1 and ν_3 stretching modes are expected to occur at frequencies higher than that of the ν_2 and ν_4 bending deformations. The appearance of two high frequency infrared bands at 473 and 392cm^{-1} suggests the C_{3v} molecular symmetry for this molecule, which is in consistence with those concluded by Hewett *et al.*[6] The assignment of the high frequency fundamentals (stretching modes) can be made on the basis of their relative intensity. For slightly non-planar molecules, one expects the $\nu_3(E)$ mode to be much more intense than $\nu_1(A_1)$. On this basis, we assign the band at 392cm^{-1} to be $\nu_1(A_1)$ and that at 473cm^{-1} to be $\nu_3(E)$. Further, the assignment of the fundamental vibrations of VCl_3 have also been confirmed by analogy with those reported for related compounds $VOCl_3$.[7,8]

However, the low frequency $\nu_2(A_1)$ and $\nu_4(E)$ bands are more difficult to assign, as no definite guidelines exist for intensity and relative magnitude of the frequencies.

It has been observed that in the case of pyramidal systems $\nu_2(A_1) < \nu_4(E)$. Hence, following the assignment of bending modes due to Wesley and Dekock,[9] Lesiecki *et al.*[10] and Hague *et al.*[11] we have assigned $\nu_2(A_1)$ mode at 160cm^{-1} and $\nu_4(E)$ to 205cm^{-1} bands. This is in agreement with the bending assignment (Cl $\hat{V}$ Cl) of $VOCl_3$ reported in literature.[7,8] The rest of the observed frequencies in Table I may be accounted for as resulting from allowed combinations or overtones of the selected four fundamentals which gives additional support for their choice.

Normal Coordinate Analysis

A normal coordinate analysis of vanadium chloride has been carried out following Wilson's **F-G** matrix method on the basis of C_{3v} point group, using a general quadratic potential function and molecular kinetic constants and a set of force constants have been reported.

The symmetry coordinates and the other details and of the procedure are the same as those given in the earlier paper.[5,12]

The kinetic constants, the force constants, the compliance constants and the mean square amplitudes of vibration at 298.16 K are given in Table II. As expected, the interaction force constants $f_{\alpha\alpha}$ and $f_{d\alpha}$ assume negative sign for this type of molecule. Further, the same sign is noted for the kinetic and potential constants in the case of bond angle interaction. The present set of force constants have been utilized in evaluating compliance constants, valence mean square amplitudes, Coriolis coupling constants and centrifugal distortion constants.

TABLE II

Values of kinetic constants (10^{-26}kg) force constants (10^2 N/M); compliance constants (10^{-2} M/N) and bonded and non-bonded mean square (10^{-3} A^2) at 298.16 K

Constants	d(V–Cl)	dd	α	$\alpha\alpha$	$d\alpha$	$d\alpha$
Kinetic contants	4.3484	0.5444	0.4843	0.0788	−0.3731	0.1962
Force contants	2.2381	0.2263	0.0587	−0.0007	−0.0392	0.0467
Compliance constants	0.4876	−0.0152	4.3882	−0.0078	0.1889	−0.1849
Bonded mean square amplitudes	2.5966	−0.2949	19.5306	−0.2818	1.0366	−0.9932
Non-bonded mean square amplitudes	σ_q 7.5374	σ_{qq} 0.9912	σ_{dq} 1.3342	σ'_{dq} 0.1011		

The compliance constants are evaluated for this molecule by Decius method.[13] These constants naturally show the trend opposite to that relating to the force constants. Using the force constant in Cyvin's secular equation[14] the symmetrized mean

square amplitude elements and hence the vibrational mean amplitudes have been obtained. From Tables III, it may be seen that the mean amplitudes for the bonded as well as the non-bonded distances obtained in the present investigation are in the characteristic range for V–Cl vibration. As expected, $l_{Cl\ldots Cl}$ is greater than l_{V-Cl}. The present set of values will be useful in the interpretation of electron-diffraction data relatingto this molecule. The present set of values for the vibrational mean amplitudesonceagain confirms the correctness of our assignment.

TABLE III

Mean amplitudes (10^{-2} A) at 298 K; Coriolis coupling constants and centrifugal distortion constant (KHz)

Mean amplitudes		Coriolis coupling constants			Centrifugal distortion contants		
l_d(V–Cl)	$\zeta^z_{3a\,3b}$	$\zeta^y_{3a\,4a}$	$\zeta^y_{1\,4_1}$	$\zeta^y_{2\,4a}$	D_J		
l_q(Cl...Cl)	$\zeta^z_{4a\,3a}$	$\zeta^y_{1\,3a}$	$\zeta^y_{2\,3a}$			D_{JK}	
	$\zeta^z_{3a\,4b}$						D_K
5.0956	0.4825	0.1786	−0.1550	0.4503	63.4088		
8.6818	−0.5463	−0.2803	0.8141			−1.0114	
	0.8201						48.3738

The first order Coriolis coupling constants of the $E \times E$ type as well as the second order constants of the type $A_1 \times E$ have been evaluated by following the matrix relation, $\zeta^\alpha = L^{-1}C^\alpha(L^{-1})^1$ making use of kinetic constants. The $C^\alpha(\alpha = x, y, z)$ matrix elements have been obtained by the vector method of Meal and Polo.[15] The Zeta values listed in Table III obey the sum rules given by Oka,[16] These values further satisfy the relations :

$$(\zeta^y_{1\,3a})^2 + (\zeta^y_{1\,4_1})^2 + (\zeta^y_{2\,3a})^2 + (\zeta^y_{2\,4_1})^2 + (\zeta^y_{3a\,4_1})^2 = 1$$

$$2[(\zeta^y_{1\,3a})^2 + (\zeta^y_{1\,4a})^2 + (\zeta^y_{2\,3a})^2 + (\zeta^y_{2\,4a})^2 - \tfrac{1}{2}] - (\zeta^z_{3a\,4b})^2 + (\zeta^z_{3a\,3b})\,(\zeta^z_{4a\,4b}) = 0$$

$$(\zeta^y_{1\,3a})\,(\zeta^y_{2\,4a}) - (\zeta^y_{1\,4a})\,(\zeta^y_{2\,3a}) = 0$$

As expected, the values of ζ^y_{13}, ζ^y_{14} and ζ^z_{44} are negative. Further, the magnitude of ζ^y_{23} and ζ^z_{34} are of the same order. The high values of the constants ζ^y_{23} and ζ^z_{34} show that the coupling concened is much stronger.

The determination of the exact rotational energy levels of a non-rigid molecule requires the knowledge of centrifugal distortion constants. The centrifugal distortion constants of vanadium chloride have been calculated by Kivelson and Wilson method[17,18] using the force constants obtained in the present investigation. They are reported in Table III. As expected, the value of D_{JK} is negative for this molecule.

The thermodynamic functions for VCl_3 have been evaluated for the ideal gas state at 1 atm assuming a rigid rotor harmonic oscillator model. The influences of spin contribution, anharmonicity and non-rigidity are neglected. The contribution to the vibrational part of these thermodynamic functions have been calculated from the tables given by Johnson *et al.*[19] The values are presented in Table IV. The constants are useful to interpret the experimental results on thermodynamic properties.

TABLE IV

Heat content, free energy, entropy and heat capacity (in cal. deg^{-1} mol^{-1}) of VCl_3, for the ideal gaseous state at 1 atmospheric pressure

$T(K)$	$(H_0 - E_0)/T$	$-(F_0 - E_0)/T$	C_p^0	S^0
273.16	13.1088	62.1273	17.5353	75.2361
298.16	13.4876	63.2864	17.8486	76.7740
300	13.5216	63.3745	17.8772	76.8961
400	14.7118	67.4147	18.6691	82.1265
500	15.5514	70.8118	19.0773	86.3632
600	16.1591	73.7161	19.3082	89.8758
700	16.6296	76.3672	19.4573	92.9968
800	16.9725	78.4364	19.5481	95.4089
900	17.2686	80.4539	19.6172	97.7225
1000	17.5072	82.2916	17.8845	99.7988

TABLE V

Potential energy distribution

Frequencies	cm^{-1}	PED (%)
ν_1	392	100 S_1
ν_2	160	100 S_2
ν_3	473	100 S_3
ν_4	205	100 S_4

The potential energy distribution evaluated for the observed fundamentals of vanadium chloride (Table V) further confirms the correctness of present assignment.

CONCLUSION

A complete vibrational analysis of vanadium chloride using the observed vibrational frequencies obtained from infrared and laser Raman studies is available on the basis of C_{3v} symmetry for the first time in the present study.

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