

## Structural and vibrational theoretical analysis of the vanadium oxotrihalides, $\text{VOX}_3$ ( $X = \text{F}, \text{Cl}, \text{Br}, \text{I}$ )

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### Abstract

A structural and vibrational theoretical study of the vanadium oxotrihalides  $\text{VOX}_3$  ( $X = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ) was performed employing ab initio (RHF) and Density Functional Theory methods. The existing vibrational data for the first three molecules were used together with the theoretical force fields to obtain the corresponding scaled force constants. The spectrum of the still unknown  $\text{VOI}_3$  was predicted using the experimental and calculated wavenumbers for the lighter molecules. The observed trends in geometrical and vibrational parameters for this series of molecules are discussed.

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**Keywords:** Vanadium oxotrihalides; Vibrational properties; Density functional theory calculations; Force constants

### 1. Introduction

Pursuing our experimental and theoretical studies on transition metal containing compounds and complementing our previous study of the  $\text{VO}_2\text{X}_2^-$  anions [1], the vanadium oxotrihalides,  $\text{VOX}_3$ , were now considered using the same theoretical approach.

Vibrational wavenumbers for  $\text{VOF}_3$  are known for the gaseous [2,3,4] and solid [5] states. Several studies were published for  $\text{VOCl}_3$  in the gaseous [4,5,6,7,8], liquid [9] and solid [10] states. The substance was also studied in  $\text{C}_6\text{H}_{12}$  solution [4] and in Ar and Kr matrices [7]; in this last study the  $^{35/37}\text{Cl}$  isotopic components were measured and the force constants calculated. The force constants for this molecule were also calculated by other authors [11,12]. The last reference includes an electron diffraction study of the molecular structure of  $\text{VOCl}_3$  (Fig. 1). The  $\text{VOBr}_3$  compound was studied spectroscopically as pure liquid [13] and solid [4], and also in  $\text{C}_6\text{H}_{12}$  solution [4].

A new route has recently been developed leading to the production of  $\text{VOX}_3$  ( $X = \text{F}, \text{Br}, \text{I}$ ) molecules from  $\text{VOCl}_3$  [14]. The authors reported low resolution, on-line, gas phase infrared spectra which show strong bands with PQR structure assigned to the VO stretching modes.

In the present work optimized geometrical structures and wavenumbers of the fundamental modes of vibration were calculated by means of quantum chemistry methods. The theoretical force fields were subsequently transformed to symmetry coordinates and adjusted to reproduce the experimental wavenumbers.

### 2. Calculations

The optimized structures and vibrational wavenumbers for  $\text{VOF}_3$ ,  $\text{VOCl}_3$ ,  $\text{VOBr}_3$  and  $\text{VOI}_3$  were obtained at the Hartree–Fock level and also by means of the Density Functional Theory (DFT) methods, using in this last case the B3LYP [15,16] and B3PW91 [15,17] functionals. Several survey calculations were made on these molecules using the 6-31G and 6-311G basis sets, as originally defined or with the addition of diffuse and/or polarization functions. In the case of  $\text{VOI}_3$  the LanL2DZ basis set, which comprises

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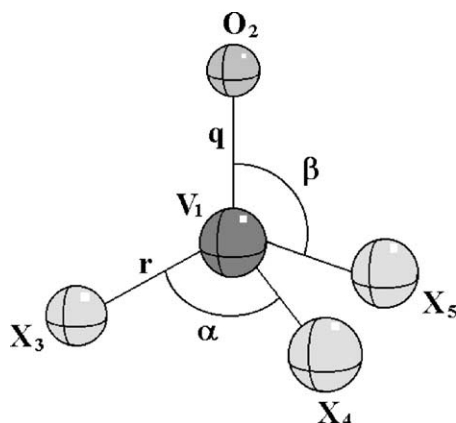


Fig. 1. Structure of the  $\text{VOX}_3$  molecules.

the iodine atom, was used. All calculations were performed with the GAUSSIAN 98 set of programs [18].

The main interest of that series of exploratory calculations was to determine which combination of method and basis set allows a good reproduction of the known vibrational wavenumbers for  $\text{VOF}_3$ ,  $\text{VOCl}_3$  and  $\text{VOBr}_3$ , meaning a good approach to the corresponding force fields. The best combination selected according with such criterium was used for the subsequent calculations. The optimized geometries and vibrational wavenumbers obtained for the  $\text{VOX}_3$  molecules using the different levels of theory and basis sets are available as detailed in Section 5.

The experimental structure determined by Karakida and Kuchitsu [12] was used as the starting structure for the geometry optimizations of the chlorine compound. No experimental data was found in the literature concerning geometrical parameters for the other oxohalides and therefore a pseudo-tetrahedral structure modeled on the HYPERCHEM program [19] was used as starting geometry in these cases. Such initial geometries were optimized at the different levels of theory until Gaussian's standard convergence criteria were fulfilled. In some cases, a startpoint structure obtained at a lower level of theory was used in order to obtain convergence.

The harmonic force fields in cartesian coordinates given by the GAUSSIAN programs were subsequently transformed to symmetry coordinates using the corresponding B matrix [20] obtained with a standard program. The resulting force field was subsequently scaled using the scheme of Pulay et al. [21], in which the main force constants are multiplied by scale factors  $f_i, f_j, \dots$  and the corresponding interaction constants are multiplied by  $(f_i f_j)^{1/2}$ , adjusting the scale factors to reproduce as well as possible the experimental wavenumbers. The potential energy distribution, which gives the contribution of each symmetry coordinate to each normal mode of vibration [20], was calculated with the resulting scaled quantum mechanics (SQM) force field.

The conversion of force constants from cartesian coordinates to symmetry coordinates, determination of

force constants factors by a least squares technique and calculation of the potential energy distribution were performed with the program FCARTP [22].

Atomic charges and Wiberg bond indexes [23] of the studied molecules were calculated by means of the Natural Bond Orbitals (NBO) approach [24], as implemented in the GAUSSIAN 98 package. Such calculations were made with the B3LYP/LanL2DZ combination, which covers the four studied molecules.

### 3. Results

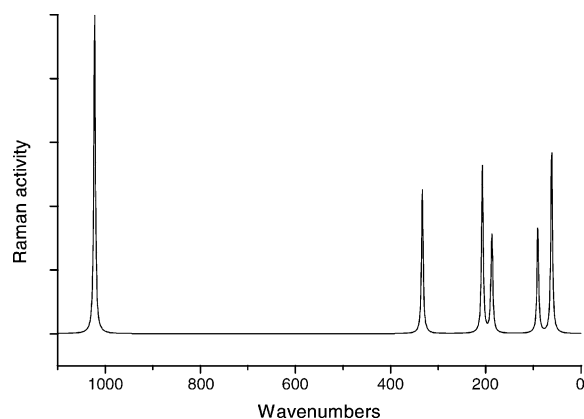
The  $\text{VOX}_3$  molecules, belonging to the  $C_{3v}$  point group, have nine normal modes of vibration which are classified as  $3A_1 + 3E$ , being all infrared and Raman active.

As mentioned before, experimental wavenumbers are known for  $\text{VOF}_3$ ,  $\text{VOCl}_3$  and  $\text{VOBr}_3$ . A comparison of these wavenumbers with the calculated ones using the different theory levels and basis sets was made by means of the root mean square deviation (RMSD) values. The exploratory calculations mentioned before allowed the selection of the B3LYP/6-31 + G combination as the one which gave the best approach to the experimental wavenumbers, giving RMSD values of 19–27  $\text{cm}^{-1}$ . DFT methods are therefore confirmed to be the most suitable to predict vibrational wavenumbers in compounds which contain transition metals [1,25,26]. It should be mentioned that, in all cases, the theoretical calculations confirmed the assignment proposed in the literature for the bands observed in the vibrational spectra.

The introduction of polarization functions in the used basis sets resulted unsatisfactory for the reproduction of the experimental wavenumbers. To have a better insight on this point, calculations on  $\text{VOF}_3$  and  $\text{VOCl}_3$  were made using the B3LYP functional and a split basis set: 6-31G\* for V and cc-pVDZ (which include polarization functions by definition) for O, F and Cl. The results, which were not better than those obtained with the above mentioned B3LYP/6-31 + G combination, appear in the tables of Section 5.

The Hartree–Fock calculations could not reproduce acceptably the known geometrical parameters for  $\text{VOCl}_3$  and specially the VO bond distance. These calculations proved also to be unsatisfactory to predict directly (that is, using no wavenumbers scaling factor) the experimentally obtained data. In fact, it was already proved by other authors that ‘...the uncorrected DFT wavenumbers and force constants approximate the experimental ones in a much more uniform fashion that does HF theory’ [27].

The vibrational wavenumbers were calculated for  $\text{VOI}_3$  using the B3LYP/LanL2DZ combination. In order to have the best possible results, these wavenumbers were adjusted using a factor calculated as the mean value of the quotients between the experimental and calculated wavenumbers for the chlorine and bromine derivatives at the same level of

Fig. 2. Theoretical Raman spectrum of the VOI<sub>3</sub> molecule.

theory. When the calculated wavenumbers for VOCl<sub>3</sub> and VOBr<sub>3</sub> were multiplied by the mentioned factor, the resulting RMSD values after comparison with the experimental wavenumbers for these two molecules were 4.0 and 3.1 cm<sup>-1</sup>, respectively. The adjusted wavenumbers of VOI<sub>3</sub> obtained in that way appear in Table 8 and are represented in Fig. 2 as a theoretical Raman spectrum using the corresponding calculated intensities.

### 3.1. Force constants

The force fields in cartesian coordinates generated by the GAUSSIAN programs for VOF<sub>3</sub>, VOCl<sub>3</sub> and VOBr<sub>3</sub> were transformed to the set of symmetry coordinates defined in Table 1. The resulting force constants were subsequently scaled according to the methodology proposed by Pulay et al. [21] (see Section 2) in order to reproduce as well as possible the experimental wavenumbers.

The calculated scale factors corresponding to each main force constant in the three molecules appear in Table 2, whereas the resulting wavenumbers and their RMSD values and potential energy distribution appear in Tables 3–5. The SQM force fields (which are also available as Supplementary Material) were used to calculate the internal force constants appearing in Table 6.

Table 1  
Definition of symmetry coordinates, according with Fig. 1

A <sub>1</sub>	$S_1 = q(1-2)$	$\nu(\text{VO})$
	$S_2 = r(1-3) + r(1-4) + r(1-5)$	$\nu_a(\text{VX}_3)$
	$S_3 = \alpha(3-1-4) + \alpha(3-1-5) + \alpha(4-1-5)$ $-\beta(2-1-3) - \beta(2-1-4) - \beta(2-1-5)$	$\delta_s(\text{OVX}_3)$
E	$S_4 = 2r(1-3) - r(1-4) - r(1-5)$	$\nu_a(\text{VX}_3)$
	$S_4' = r(1-4) - r(1-5)$	$\nu_a(\text{VX}_3)$
	$S_5 = 2\beta(2-1-3) - \beta(2-1-4) - \beta(2-1-5)$	$\rho(\text{OVX}_3)$
	$S_5' = \beta(2-1-4) - \beta(2-1-5)$	$\rho(\text{OVX}_3)$
	$S_6 = 2\alpha(4-1-5) - \alpha(3-1-5) - \alpha(3-1-4)$	$\delta_a(\text{VX}_3)$
	$S_6' = \alpha(3-1-5) - \alpha(3-1-4)$	$\delta_a(\text{VX}_3)$

Table 2  
Scale factors for the force field of VOX<sub>3</sub> (X = F, Cl, Br)

Coordinate	Factor		
	VOF <sub>3</sub>	VOCl <sub>3</sub>	VOBr <sub>3</sub>
$\nu(\text{VO})$	0.917	0.918	0.896
$\nu_a(\text{VF}_3)$	1.041	1.027	0.876
$\nu_s(\text{VF}_3)$	1.065	1.062	0.876
$\rho(\text{OVF}_3)$	1.065	0.976	1.006
$\delta_s(\text{VF}_3)$	1.120	1.062	1.571
$\delta_a(\text{VF}_3)$	1.120	1.027	1.571

$\nu$ , stretching;  $\delta$ , deformation;  $\rho$ , rocking.

The obtained SQM force field (in symmetry coordinates) for VOCl<sub>3</sub> is compared with previous results in Table 7. A rather good agreement is observed between the four sets of main force constants. Considering the complete sets of force constants the best agreements appear between the values calculated in the present work and those corresponding to the A<sub>1</sub> modes of Ref. [12] and the E modes of Ref. [11].

## 4. Discussion of the results

The experimental wavenumbers measured for the VOX<sub>3</sub> molecules are gathered in Table 8, which also include the predicted wavenumbers for the still unknown iodine compound. Some calculated distances, angle and valence force constants were also included in the Table to facilitate the discussion.

A monotonic decrease of wavenumbers is observed along the series. The decrease in VO stretching wavenumbers and the corresponding force constants follow the same trend showed by the Wiberg indexes. The VO distances, however, show an irregular trend with a minimum value for the chlorine compound, also observed in calculations made with different basis sets.

The increasing halogen covalent radius along the series is reflected in the VX calculated distances and the decreasing values of the associated force constants and stretching wavenumbers. The Wiberg indexes, however, show an increasing trend which can be explained qualitatively taking into account the resonance structures for the VOX<sub>3</sub> molecules shown in Fig. 3. The equivalent structures II, III and IV should become more important for the heavier, less electronegative halogen atoms, for which a more positive charge should be expected along the series. In fact, these calculated charges are: F, -0.39; Cl, -0.11; Br, -0.04; I; ca. 0.0. Besides, the displacement of negative charge towards the central vanadium atom should reduce its positive charge, which, effectively, varies in the order VOF<sub>3</sub>, 1.52; VOCl<sub>3</sub>, 0.55; VOBr<sub>3</sub>, 0.37; VOI<sub>3</sub>, 0.26. These charge trends should be accompanied by an increase of the VX bond order and a decrease of the VO bond order, again

Table 3

Observed and calculated wavenumbers ( $\text{cm}^{-1}$ ), infrared and Raman intensities, potential energy distribution and assignments for  $\text{VOF}_3$ 

Symmetry species	Mode	Observed <sup>a</sup>	Calculated <sup>b</sup>	Calc. SQM <sup>c</sup>	IR intens. <sup>d</sup>	Raman activ. <sup>e</sup>	PED (>10%)	Assignments
$A_1$	1	1057.8	1102	1058	152.9	16.9	98 S <sub>1</sub>	$\nu$ (VO)
	2	721.5	700	722	38.6	15.9	96 S <sub>2</sub>	$\nu_s$ ( $\text{VF}_3$ )
	3	257.8	243	256	13.9	2.24	99 S <sub>3</sub>	$\delta_s$ ( $\text{VF}_3$ )
$E$	4	806.0	789	806	193.1	2.63	96 S <sub>4</sub>	$\nu_a$ ( $\text{VF}_3$ )
	5	308.0	298	308	6.76	3.30	95 S <sub>5</sub>	$\rho$ ( $\text{OVF}_3$ )
	6	204.3	194	205	8.04	2.61	98 S <sub>6</sub>	$\delta_a$ ( $\text{VF}_3$ )
RMSD ( $\text{cm}^{-1}$ )			22.7	1.04				

 $\nu$ , stretching;  $\delta$ , deformation;  $\rho$ , rocking.<sup>a</sup> From Ref. [3].<sup>b</sup> From B3LYP/6-31 + G calculation.<sup>c</sup> From scaled quantum mechanics force field.<sup>d</sup> Units are  $\text{km mol}^{-1}$ .<sup>e</sup> Raman activities in  $\text{\AA}^4 (\text{amu})^{-1}$ .

Table 4

Observed and calculated wavenumbers ( $\text{cm}^{-1}$ ), infrared and Raman intensities, potential energy distribution and assignments for  $\text{VOCl}_3$ 

Symmetry species	Mode	Observed <sup>a</sup>	Calculated <sup>b</sup>	Calc. SQM <sup>c</sup>	IR intens. <sup>d</sup>	Raman activ. <sup>e</sup>	PED (>10%)	Assignments
$A_1$	1	1042.5	1087	1043	133.2	22.1	99 S <sub>1</sub>	$\nu$ (VO)
	2	409.5	399	409	8.70	27.5	103 S <sub>2</sub>	$\nu_s$ ( $\text{VCl}_3$ )
	3	163.0	160	164	1.30	4.92	98 S <sub>3</sub>	$\delta_s$ ( $\text{VCl}_3$ )
$E$	4	503.0	498	503	118.7	5.01	102 S <sub>4</sub>	$\nu_a$ ( $\text{VCl}_3$ )
	5	248.0	249	246	0.187	4.52	91 S <sub>5</sub>	$\rho$ ( $\text{VCl}_3$ )
	6	124.5	125	125	0.300	6.60	97 S <sub>6</sub>	$\delta_a$ ( $\text{VCl}_3$ )
RMSD ( $\text{cm}^{-1}$ )			18.9	0.62				

 $\nu$ , stretching;  $\delta$ , deformation;  $\rho$ , rocking.<sup>a</sup> From Ref. [4].<sup>b</sup> From B3LYP/6-31 + G calculation.<sup>c</sup> From scaled quantum mechanics force field.<sup>d</sup> Units are  $\text{km mol}^{-1}$ .<sup>e</sup> Raman activities in  $\text{\AA}^4 (\text{amu})^{-1}$ .

Table 5

Observed and calculated wavenumbers ( $\text{cm}^{-1}$ ), infrared and Raman intensities, potential energy distribution and assignments for  $\text{VOBr}_3$ 

Symmetry species	Mode	Observed <sup>a</sup>	Calculated <sup>b</sup>	Calc. SQM <sup>c</sup>	IR intens. <sup>d</sup>	Raman activ. <sup>e</sup>	PED (>10%)	Assignments
$A_1$	1	1025.0	1082	1025	131.4	22.3	99 S <sub>1</sub>	$\nu$ (VO)
	2	271.0	282	269	2.82	16.5	87 S <sub>2</sub>	$\nu_s$ ( $\text{VBr}_3$ )
	3	120.0	97	118	0.058	4.23	91 S <sub>3</sub> + 13 S <sub>2</sub>	$\delta_s$ ( $\text{VBr}_3$ )
$E$	4	400.0	420	401	84.5	3.24	80 S <sub>4</sub> + 16 S <sub>5</sub>	$\nu_a$ ( $\text{VBr}_3$ )
	5	212.0	214	212	0.01	3.36	83 S <sub>5</sub> + 15 S <sub>4</sub>	$\rho$ ( $\text{OVBr}_3$ )
	6	83.0	68	84	0.00	4.41	96 S <sub>6</sub>	$\delta_a$ ( $\text{VBr}_3$ )
RMSD ( $\text{cm}^{-1}$ )			27.0	1.12				

 $\nu$ , stretching;  $\delta$ , deformation;  $\rho$ , rocking.<sup>a</sup> From Ref. [13].<sup>b</sup> From B3LYP/6-31 + G calculation.<sup>c</sup> From scaled quantum mechanics force field.<sup>d</sup> Units are  $\text{km mol}^{-1}$ .<sup>e</sup> Raman activities in  $\text{\AA}^4 (\text{amu})^{-1}$ .

Table 6  
Internal force constants for VOX<sub>3</sub> molecules

Force constant	VOF <sub>3</sub>	VOCl <sub>3</sub>	VOBr <sub>3</sub>
<i>f</i> (VO)	7.87	7.73	7.47
<i>f</i> (VEX)	4.87	2.67	2.13
<i>f</i> (VO/VX)	0.26	0.18	0.16
<i>f</i> (VX/VX)	0.23	0.14	0.09
<i>f</i> (OVX)	0.68	0.58	0.53
<i>f</i> (XVX)	0.43	0.41	0.41

Units are mdyn Å<sup>-1</sup> for bond stretchings and mdyn Å rad<sup>-2</sup> for angle deformations.

Table 7  
Comparison of the symmetry force constants for VOCl<sub>3</sub> with results obtained by other authors<sup>a</sup>

	This work	Ref. [7]	Ref. [12]	Ref. [11]
<i>A</i> <sub>1</sub>				
<i>F</i> <sub>1,1</sub> (ν VO)	7.73	7.94	7.72	7.64
<i>F</i> <sub>1,2</sub>	0.315	1.06	0.20	0.008
<i>F</i> <sub>1,3</sub>	0.101	0.0	0.077	-0.0254
<i>F</i> <sub>2,2</sub> (ν VCl <sub>3</sub> symm.)	2.95	3.08	3.01	3.036
<i>F</i> <sub>2,3</sub>	-0.0425	0.0	0.0	0.0297
<i>F</i> <sub>3,3</sub> (δ VCl <sub>3</sub> symm.)	0.647	0.63	0.625	0.700
<i>E</i>				
<i>F</i> <sub>4,4</sub> (ν VCl <sub>3</sub> asymm.)	2.53	2.44	2.07	2.591
<i>F</i> <sub>4,5</sub>	0.030	0.12	-0.13	0.0528
<i>F</i> <sub>4,6</sub>	0.0	0.24	0.16	-0.0276
<i>F</i> <sub>5,5</sub> (ρ OVCl <sub>3</sub> )	0.702	0.66	0.78	0.685
<i>F</i> <sub>5,6</sub>	-0.0298	-0.11	-0.19	0.00397
<i>F</i> <sub>6,6</sub> (δ VCl <sub>3</sub> asymm.)	0.460	0.55	0.52	0.439

Units are mdyn Å<sup>-1</sup> for bond stretchings and mdyn Å rad<sup>-2</sup> for angle deformations.

Table 8  
Experimental wavenumbers and additional calculated data for the VOX<sub>3</sub> molecules

	VOF <sub>3</sub>	VOCl <sub>3</sub>	VOBr <sub>3</sub>	VOI <sub>3</sub> <sup>a</sup>
ν VO	1057.8	1042.5	1025.0	1022 (1025)
ν <sub>a</sub> VX <sub>3</sub>	806.0	503.0	400.0	333
ν <sub>s</sub> VX <sub>3</sub>	721.5	409.5	271.0	207
ρ OVX <sub>3</sub>	308.0	246.0	212.0	187
δ <sub>s</sub> VX <sub>3</sub>	257.8	163.0	120.0	91
δ <sub>a</sub> VX <sub>3</sub>	204.3	124.5	83.0	62
<i>d</i> VO (Å) <sup>b</sup>	1.575	1.571	1.572	1.574
<i>f</i> VO (mdyn.Å <sup>-1</sup> )	7.87	7.73	7.47	-
<i>WI</i> VO <sup>b</sup>	2.140	2.135	2.118	2.115
<i>d</i> VX (Å) <sup>b</sup>	1.734	2.168	2.331	2.532
<i>f</i> VX (mdyn.Å <sup>-1</sup> )	4.87	2.67	2.13	-
<i>WI</i> VX <sup>b</sup>	0.879	1.120	1.150	1.159
α XVX (deg.) <sup>b</sup>	110.9	110.9	111.0	111.0

ν, stretching; δ, angular deformation; ρ, rocking; *d*, distance; *f*, force constant; *WI*, Wiberg index.

<sup>a</sup> Calculated values (see text). Observed value [14] in parentheses.

<sup>b</sup> Calculated with B3LYP/LanL2DZ.

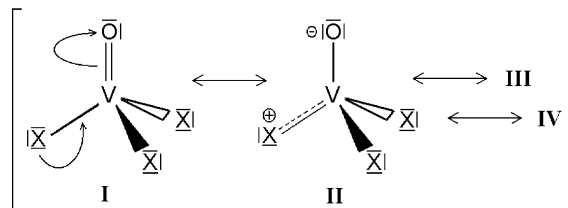


Fig. 3. Resonant structures of the VOX<sub>3</sub> molecules.

along the series, as confirmed by the Wiberg indexes of Table 8.

A final observation refers to the constancy of the XVX angles, as shown in Table 8 and observed also in the calculations made with different theory levels and basis sets.

## 5. Supplementary material

Tables containing the structural and vibrational results obtained with the different levels of theory and basis sets as well as the SQM matrices of force constants for the studied molecules are available in the following Internet site: [www.quimica.unlp.edu.ar/cequinor/varetti/VOX3.pdf](http://www.quimica.unlp.edu.ar/cequinor/varetti/VOX3.pdf)

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