Mean Amplitudes of Vibration of the $VO_2F_2^-$ and $VO_2Cl_2^-$ Anions

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Abstract

The mean amplitudes of vibration of the $VO_2F_2^-$ and $VO_2Cl_2^-$ anions, derived from vanadium (V), were calculated from known spectroscopic and structural data, in the temperature range between 0 K and 1000 K. The results are discussed and compared with those of the isoelectronic chromium (VI) species CrO_2F_2 and CrO_2Cl_2 and with those of other simple vanadium compounds.

Keywords: $VO_2F_2^-$; $VO_2Cl_2^-$; Mean amplitudes of vibration; Isoelectronic Cr (VI) species; Bond properties

Introduction

Mean amplitudes of vibration are very useful and valuable parameters for the analysis of molecular structures and their vibrational behaviour. Mean amplitudes of vibration can be derived directly from electron-diffraction experiments and can also be obtained by calculation from vibrational spectroscopic data. Precisely, the starting point of the spectroscopic calculations was their usefulness in the analysis and interpretation of electron-diffraction spectra [1,2]. In order to extend our knowledge on the vibrational properties of vanadium halides and oxyhalides, we have now performed a calculation of the mean amplitudes of vibration of the two anionic oxyhalides $VO_2F_2^-$ and $VO_2Cl_2^-$. These two interesting anions, are the only so far known vanadium (V) species of the type $VO_2X_2^-$, and are isoelectronic to the better known and widely studied chromium (VI) oxyhalides, CrO_2F_2 and CrO_2Cl_2. The two vanadium-anions can be isolated in the form of their tetraphenyl arsonium and tetra-phenyl phosphonium salts [3,4] and also the triphenyl-methyl phosphonium salt is known [5]. Crystallographic and spectroscopic studies of these salts ensure the presence of the "free" C_{2v} $VO_2X_2^-$ species in the respective crystal lattices [3-5]. The detailed assignment of the vibrational (IR and Raman) spectra of both anions, supported by the calculation of the corresponding force constants was performed some years ago by Brandán et al. [6]. We have now extended and complemented this interesting work with the calculation of the respective mean amplitudes of vibration, in a wide temperature range.

Calculations

The calculations of the mean amplitudes of vibration were performed with the method of the "Characteristic Vibrations" of Müller et al. [7,8]. As known, in this method the investigated molecule, of any degree of complexity, is divided in

"fragments" of the type XY_2 or ZXY and vibrational frequencies are assigned to these "pseudo molecules" with which all further calculations are performed. This means that any problem of a determined degree of complexity (n) is reduced to the resolution of problems of order n = 2 (fragments XY2) and n = 3 (fragments ZXY).

This methodology has been applied with great success to a wide number of molecules and ions during the last forty years (for a recent review see for example [9]) and can be considered as a very straightforward methodology for this type of calculations.

For the present calculations the necessary vibrational-spectroscopic data as well as the structural parameters were taken from the paper of Brandán et al. [6].

Results and Discussion

The obtained results, in the temperature range between 0 and 1000 K, are shown in TABLES 1 and 2.

TABLE 1. **Calculated mean amplitudes of vibration (in Å) of the $VO_2F_2^-$ anion**

T (K)	u_{V-O}	u_{V-F}	$u_{O...O}$	$u_{F...F}$	$u_{O...F}$
0	0.0379	0.0433	0.063	0.071	0.062
100	0.0379	0.0433	0.064	0.074	0.063
200	0.0379	0.0437	0.067	0.085	0.069
298.16	0.0382	0.0452	0.072	0.097	0.077
300	0.0382	0.0453	0.073	0.097	0.077
400	0.0391	0.0477	0.079	0.109	0.086
500	0.0403	0.0506	0.086	0.12	0.094
600	0.0418	0.0536	0.092	0.131	0.102
700	0.0435	0.0567	0.098	0.141	0.109
800	0.0453	0.0598	0.104	0.15	0.116
900	0.0471	0.0627	0.11	0.158	0.122
1000	0.0489	0.0656	0.115	0.167	0.129

TABLE 2. **Calculated mean amplitudes of vibration (in Å) of the $VO_2Cl_2^-$ anion**

T (K)	u_{V-O}	u_{V-Cl}	$u_{O...O}$	$u_{Cl...Cl}$	$u_{O...Cl}$
0	0.0379	0.0431	0.065	0.07	0.073
100	0.0379	0.0432	0.065	0.08	0.075
200	0.0379	0.045	0.07	0.101	0.088
298.16	0.0383	0.0488	0.076	0.12	0.101
300	0.0383	0.0488	0.077	0.121	0.101
400	0.0391	0.0533	0.084	0.138	0.114
500	0.0403	0.0579	0.091	0.153	0.126
600	0.0419	0.0623	0.098	0.168	0.137
700	0.0436	0.0666	0.105	0.181	0.147
800	0.0453	0.0707	0.112	0.193	0.157

| 900 | 0.0471 | 0.0746 | 0.118 | 0.205 | 0.166 |
| 1000 | 0.0489 | 0.0784 | 0.124 | 0.215 | 0.175 |

A first analysis of these results shows that the mean amplitude values for the V=O bonds are practically identical in both anions whereas those of the V-F bonds are slightly lower than those of the V-Cl bonds. These results are in agreement with the force constants determined for these bonds. In both anions, the force constants for the V=O bonds are nearly the same (6.56 mdyn/Å for $VO_2F_2^-$ and 6.59 mdyn/Å for $VO_2Cl_2^-$) [6], whereas those for the V-X bonds are somewhat stronger for the fluoride (3.49 mdyn/Å for $VO_2F_2^-$ and 2.33 mdyn/Å for $VO_2Cl_2^-$) [6].

This general behaviour is similar to that found for the isoelectronic chromium(VI) molecules, *i.e.* CrO_2Cl_2 [10] and CrO_2F_2 [11]. For the chromyl fluoride the Cr=O mean amplitude values are practically identical than those of the analogous bonds of chromyl chloride, whereas the amplitude values for the Cr-F bonds are clearly lower than those corresponding to the Cr-Cl bonds. This means that in both pair of isoelectronic species the M=O bonds have practically the same strength, whereas the M-X bonds are slightly stronger in the case of the fluorides. A comparison of the calculated values for the two isoelectronic pairs, at four selected temperatures is shown in TABLE 3. In all cases and as expected, bonds of the neutral chromium species are slightly stronger than those of the corresponding anionic vanadium species.

TABLE 3. **Comparison of the mean amplitudes of vibration (in Å) of the two isoelectronic pairs, at some selected temperatures**

T (K)	$VO_2F_2^-$		CrO_2F_2	
	u_{V-O}	u_{V-F}	u_{Cr-O}	u_{Cr-F}
0	0.0379	0.0433	0.0369	0.0399
298.16	0.0382	0.0452	0.0372	0.041
600	0.0418	0.0536	0.0403	0.047
1000	0.0489	0.0656	0.0468	0.0566
	$VO_2Cl_2^-$		CrO_2Cl_2	
	u_{V-O}	u_{V-Cl}	u_{Cr-O}	u_{Cr-Cl}
0	0.0379	0.0431	0.0373	0.0407
298.16	0.0382	0.0488	0.0376	0.0449
600	0.0419	0.0623	0.041	0.0563
1000	0.0489	0.0784	0.0477	0.0704

For the mean amplitudes of the non-bonded atomic pairs it is more difficult to made theoretical predictions of their relative values, as they are often strongly dependent on minimal geometric differences and on mass effects which are difficult to evaluate. Notwithstanding, it is interesting to remark that in the present case all the deformational modes of the cholorovanadate are at slightly lower energies than those of the fluorovanadate [6], suggesting that probably somewhat higher mean amplitudes of vibration for the non-bonded pairs can be expected for $VO_2Cl_2^-$, as found. The values obtained for the two investigated anions lie in the order $u_{O-O} < u_{O-X} < u_{X-X}$ for both species, at all temperatures above 200 K, and the absolute values are always higher in the case of $VO_2Cl_2^-$, as mentioned. As it is known, mean amplitudes of vibration can be very characteristic for a given chemical bond [8]. This means that if the stretching force constant and the corresponding

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frequency for a definite bond in different molecules are nearly the same, this will also be true for mean amplitudes of vibration [8,12]. Therefore, it seems interesting to compare the present results with those obtained for other vanadium species containing V-oxygen and/or vanadium-halogen bonds. Some data are presented in TABLE 4 [13-15].

TABLE 4. **Mean amplitudes of vibration (in Å), at 298 K, for V-O, V-F and V-Cl bonds in different molecular and anionic species Species V-O bond V-F bond V-Cl bond Reference**

Species	V-O bond	V-F bond	V-Cl bond	Reference
VO_4^{3-}	0.042			[13]
$VO_2F_2^-$	0.0382	0.0452		this paper
VO_2Cl_2-	0.0383		0.0488	this paper
VOF_3	0.0366	0.0404		[8,14]
$VOCl_3$	0.0369		0.0459	[8,14]
$VOBr_3$	0.0371			[8,14]
VCl_4			0.0471	[8]
VF_5		0.0415 (ax.)		[8,15]
VF_5		0.0405 (eq.)		[8,15]

As it can be seen, the mean amplitudes of vibration for V-O bonds lie in a very limited range, between 0.037 Å and 0.042 Å with the anionic species presenting slightly higher values than the neutral ones. Also, in the case of the V-X bonds the mean amplitude values are found in relatively restricted ranges. Interestingly, and despite the different oxidation state, the V-Cl value calculated for the vanadium (IV) VCl_4 species is comparable with those found for the two tabulated V (V) species.

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