Mean Amplitudes of Vibration of Chlorosyl Fluoride, FClO

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Mean amplitudes of vibration of the FClO molecule have been calculated from recently reported vibrational spectroscopic data in the temperature range between 0 and 1000 K. The results are briefly discussed and some comparisons with related species are made.

Key words: Chlorosyl Fluoride; Mean Amplitudes of Vibration; Bond Properties.

Five of the six possible oxide fluorides of chlorine have been characterized. They range in stability from the thermally unstable chlorosyl fluoride, FClO, to the chemically rather inert perchloryl fluoride, $FClO_3$ [1].

FClO is a very interesting molecule as it consists of a hypervalent chlorine atom bonded to the two most electronegative atoms, fluor and oxygen, in an angular, C_s-symmetry, arrangement. It can be obtained by controlled hydrolysis of ClF_3 in a flow reactor or by photolysis of a mixture of ClF and O_3 in an argon matrix [2].

As a part of our current studies on vibrational properties of compounds with interhalogen bonds and related species, we have now undertaken the calculation of mean amplitudes of vibration of this molecule.

The necessary vibrational-spectroscopic data and the structural parameters were taken from a recently performed high resolution FTIR spectroscopy study [3].

The mean amplitudes of vibration were calculated using the "Method of the Characteristic Vibrations" of A. Müller and coworkers [4, 5] (cf. also [6]).

The obtained mean amplitudes of vibration, in the temperature range between 0 and 1000 K, are shown in Table 1. These results clearly confirm the existence of a relatively strong Cl–O bond and a weaker Cl–F bond, reflected in higher mean amplitude values and in stronger temperature dependence.

Such a behavior is relatively usual for this type of hypervalent species, since the generation of a strong chlorine-oxygen bond generates a semi-ionic and relatively weak Cl–F bond. In the present molecule, this is also revealed by the very different force constants of the two bonds, the values of which are of 7.01 mdyn/Å for the Cl–O bond and only of 2.51 mdyn/Å for the Cl–F bond [3].

As it seems interesting to make some comparisons with other related species, in Table 2 we present mean amplitude values and force constants for the Cl–F bonds in a series of molecules and ions. Generally speaking, there exists a fairly good correlation between the force constant- and mean amplitude-values, i.e. stronger force constants generate lower mean amplitudes of vibration. The data of Table 2 also point to a diminution of the ionic (or semi ionic) bond character in going from $ClO_2F_2^-$ to ClF_2^+. The $ClO_2F_2^-$ anion represents an extreme case, in which the two axial Cl–F bonds can practically be described as semi-ionic $p-\sigma$ bonds, i.e., 3-center-4-electron (3c – 4e) bonds [7, 8]. The molecule ClF and the ClF_2^+ cation, with very short and strongly covalent bonds, represent the other limiting type of Cl–F bond.

Table 1. Mean amplitudes of vibration (Å) for FClO.

T (K)	u_{Cl-O}	u_{Cl-F}	$u_{F\cdots O}$
0	0.0383	0.0476	0.057
100	0.0384	0.0476	0.057
200	0.0384	0.0483	0.061
298.16	0.0386	0.0504	0.068
300	0.0386	0.0504	0.068
400	0.0393	0.0535	0.075
500	0.0404	0.0570	0.082
600	0.0417	0.0607	0.088
700	0.0432	0.0644	0.094
800	0.0448	0.0679	0.100
900	0.0465	0.0714	0.106
1000	0.0482	0.0748	0.111

Table 2. Force constants (mdyn/Å) and mean amplitudes of vibration (in Å, and at 298 K) for Cl–F bonds in different molecules and ions.

Species	f_{Cl-F}	Ref.	u_{Cl-F}	Ref.
$ClO_2F_2^-$	1.60	[7]	0.0622	[8]
ClF_4O^-	1.838	[9]	0.0555	[10]
ClF_2^-	1.864	[11]	0.0595	[12]
ClF_4^-	2.13	[13]	0.0560	[14]
FClO	2.51	[3]	0.0504	this work
$FClO_2$	2.53	[15]	0.0487	[16]
ClF	4.36	[17]	0.0430	[17]
ClF_2^+	4.74	[18]	0.0416	[19]

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All these comparisons suggest that in FClO this bond is of an intermediate type, but evidently closer to a semi-ionic one.

On the other hand, and as it can also be seen from Table 2, the mean amplitude values for this bond cover a relatively broad range between 0.0622 and 0.0416 Å.

This behavior contrasts with those of the Cl–O bonds, which for the oxygenated species shown in Table 2, extend only between 0.0386 Å (FClO) to 0.0358 Å (ClF_4O^-), despite the fact that the corresponding Cl–O force constants are rather different (7.01 mdyn/Å for FClO [3] and 9.38 mdyn/Å for ClF_4O^- [9]). This means that the mean amplitudes of vibration are more characteristic [5] for the Cl–O than for the Cl–F bonds. This statement is additionally supported by the fact that also the mean amplitudes of other species containing this bond lie in the same range (for example: ClO_2: 0.0385 Å; ClO_4^-: 0.038 Å and ClO_3^-: 0.040 Å, at 298 K [5]).

Regarding the mean amplitudes of vibration for the non bonded O···F pair of FClO they show, as usual, a relatively important temperature dependence (cf. Table 1). They are comparable to those calculated for the similar non-bonded pair in the $FClO_2$ molecule [16].

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