

## Mean Amplitudes of Vibration of F<sub>3</sub>ClO

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Mean amplitudes of vibration of F<sub>3</sub>ClO have been calculated from vibrational spectroscopic data in the temperature range between 0 and 1000 K. Its bond properties are discussed on the basis of the obtained results and by comparison with known data for related species. Mean amplitudes of vibration for the related F<sub>3</sub>BrO molecule are also estimated and briefly discussed

*Key words:* F<sub>3</sub>ClO; F<sub>3</sub>BrO; Mean Amplitudes of Vibration; Bond Properties

As a continuation of our studies devoted to the vibrational and bond properties of molecules and ions containing interhalogen or halogen-oxygen bonds we have now performed an analysis of the bond characteristics of chlorine trifluoride oxide (chlorosyl trifluoride, F<sub>3</sub>ClO), through a calculation of its mean amplitudes of vibration from spectroscopic data.

The interesting F<sub>3</sub>ClO molecule has been obtained by either direct fluorination of Cl<sub>2</sub>O, NaClO<sub>2</sub> or ClONO<sub>2</sub> or by glow discharge of F<sub>2</sub> in the presence of solid Cl<sub>2</sub>O [1]. Its vibrational (IR and Raman) spectra are consistent with a trigonal bipyramidal structure around the chlorine atom (C<sub>s</sub>-symmetry) containing the oxygen atom, one fluorine atom and a lone pair in the equatorial plane and the other two fluorine atoms in axial positions [2].

The mean amplitudes of vibration were calculated by the method of the characteristic vibrations of Müller et al. [3] (cf. also [4, 5]). The necessary vibrational frequencies were taken from the paper of Christe and Curtis [2] and the following geometric parameters were used:  $d(\text{Cl-O}) = 1.42 \text{ \AA}$ ,  $d(\text{Cl-F}(\text{eq})) = 1.62 \text{ \AA}$ ,  $\angle \text{OCIF}(\text{eq}) = 120^\circ$  and  $\angle \text{F}(\text{ax})\text{Cl}(\text{F}(\text{ax})) = 180^\circ$  [2].

The results of the calculations, in the temperature range between 0 and 1000 K are shown in Table 1.

As it can be seen, the Cl–O bond is particularly strong, as reflected by the relatively low mean amplitude values and its weak temperature dependence. On the other hand, and as expected for a multiple halogen-oxygen bond, this linkage shows a very characteristic

Table 1. Calculated mean amplitudes of vibration (in Å) of F<sub>3</sub>ClO.

<i>T</i> (K)	<i>u</i> <sub>Cl–O</sub>	<i>u</i> <sub>Cl–F(eq)</sub>	<i>u</i> <sub>Cl–F(ax)</sub>	<i>u</i> <sub>F...O</sub>	<i>u</i> <sub>F(ax)...F(ax)</sub>
0	0.0357	0.0443	0.0477	0.046	0.061
100	0.0357	0.0443	0.0478	0.046	0.061
200	0.0357	0.0446	0.0486	0.047	0.063
298.16	0.0359	0.0459	0.0509	0.049	0.067
300	0.0359	0.0459	0.0509	0.049	0.067
400	0.0363	0.0481	0.0542	0.052	0.073
500	0.0370	0.0508	0.0579	0.055	0.078
600	0.0380	0.0536	0.0616	0.059	0.084
700	0.0391	0.0566	0.0654	0.062	0.090
800	0.0403	0.0595	0.0691	0.066	0.095
900	0.0417	0.0624	0.0726	0.069	0.100
1000	0.0430	0.0652	0.0760	0.072	0.105

mean amplitude of vibration. It is comparable with values calculated, at 298 K, for other chlorine (V) species, for example 0.0358 Å in ClF<sub>4</sub>O<sup>–</sup> [6], 0.0360 Å in ClO<sub>2</sub>F [7] and 0.0366 Å in ClO<sub>2</sub>F<sub>2</sub><sup>–</sup> [8], and is even slightly lower than in the ClO<sub>3</sub><sup>–</sup> anion (0.040 Å) [4]. Interestingly, this bond also presents a very high force constant (9.37 mdyne/Å) [2].

The values calculated for the Cl–F bonds reflect a slightly different behaviour of these two geometrically different interhalogen bonds. The equatorial Cl–F bond is somewhat stronger than the two axial ones, as reflected by its lower mean amplitude value and weaker temperature dependence. This finding is in agreement with the respective force constants (3.16 mdyne/Å for the Cl–F(eq) bond and 2.34 mdyne/Å for the Cl–F(ax) bonds [2]). The force constant for the axial bonds is identical with that previously calculated for ClF<sub>2</sub><sup>–</sup> [9]. Consequently, this linkage also shows a similar mean amplitude in both species, although the overall bond strength is slightly lower in the anion (mean amplitude of vibration of the Cl–F bond in ClF<sub>2</sub><sup>–</sup> is 0.0595 Å at 298.16 K [10], probably due to the lower oxidation state of chlorine and the presence of the negative charge.

On the other hand, the two sets of Cl–F amplitude values show that these bonds are slightly stronger than in ClO<sub>2</sub>F<sub>2</sub><sup>–</sup> (0.0622 Å at 298 K) [8] and in ClF<sub>4</sub>O<sup>–</sup> (0.0555 Å at 298 K) [6] and are comparable to that in ClO<sub>2</sub>F (0.0487 Å at 298 K [7]). Interestingly, the amplitude of the Cl–F(eq) bond is comparable to that calculated for the two Cl–F(axial) bonds in ClF<sub>4</sub><sup>+</sup> (0.0458 Å at 298 K), but both Cl–F bonds in F<sub>3</sub>ClO are somewhat weaker than the respective equatorial bonds of the men-

tioned cation (0.0417 Å at 298 K) [11]. These comparisons show again that the Cl–F bonds are not as characteristic as the Cl–O bonds, and that they are more dependent on geometrical peculiarities.

Besides, all the commented findings agree with the expected structural characteristics of the F<sub>3</sub>ClO molecule. As mentioned before, high mean amplitude values and important temperature dependencies are typical for very weak interhalogen bonds [10], and this behaviour can be rationalized in terms of the semi-ionic three-center four-electron bond model [12–14]. This is apparently the behaviour of the axial Cl–F bonds in F<sub>3</sub>ClO and, in this case, the ionic character of these axial bonds may be additionally enhanced by the presence of the commented strong Cl–O bond, in a similar way as previously discussed in the case of ClO<sub>2</sub>F<sub>2</sub><sup>−</sup> [8, 15]. Summarizing, the overall bonding characteristics in F<sub>3</sub>ClO may be described in the following way: the bonding of the three equatorial ligands (including the lone pair and ignoring the second bond of the Cl=O double bond) mainly involves a sp<sup>2</sup> hybrid of the chlorine atom, whereas the bonding of the two axial Cl–F bonds mainly involves the remaining p orbital, which generates the commented semiionic three-center for-electron pσ bond.

To complement this study, we have also made an estimation of the mean amplitudes of vibration of the related F<sub>3</sub>BrO molecule. This compound has been obtained by reaction of KBrF<sub>4</sub>O with HF [16] or by treatment of KBrF<sub>4</sub>O with O<sub>2</sub>AsF<sub>6</sub> [17]. An analysis of its IR and Raman spectra suggests that, although it is not monomeric, it possess a similar structure as F<sub>3</sub>ClO, involving some kind of molecular association. The association apparently involves mainly the Br–F(ax) bonds, whereas the Br=O bond is not involved [16].

The mean amplitudes of vibration were calculated with the same procedure as above, using the available spectroscopic data [16, 17] and the following estimated geometrical parameters:  $d(\text{Br–O}) = 1.55 \text{ \AA}$ ,  $d(\text{Br–F}(\text{eq})) = 1.73 \text{ \AA}$ ,  $\angle \text{OBrF}(\text{eq}) = 120^\circ$  and  $\angle \text{F}(\text{ax})\text{Br}(\text{F}(\text{ax})) = 180^\circ$ . The obtained results, which should be analyzed

Table 2. Estimated mean amplitudes of vibration (in Å) of F<sub>3</sub>BrO at some selected temperatures.

$T(\text{K})$	$u_{\text{Br–O}}$	$u_{\text{Br–F}(\text{eq})}$	$u_{\text{Br–F}(\text{ax})}$	$u_{\text{F}\cdots\text{O}}$	$u_{\text{F}(\text{ax})\cdots\text{F}(\text{ex})}$
0	0.0356	0.0420	0.0445	0.055	0.060
298.16	0.0359	0.0442	0.0478	0.062	0.066
500	0.0377	0.0498	0.0549	0.072	0.077
1000	0.0455	0.0650	0.0727	0.097	0.104

with caution due to the commented molecular association, are shown in Table 2 at four selected temperatures.

As it can be seen, the two sets of Br–F mean amplitude values differ less than the corresponding pairs in F<sub>3</sub>ClO, although also in this case the axial bonds are weaker than the equatorial ones. On the other hand, these Br–F bonds appear to be somewhat stronger than in BrO<sub>2</sub>F<sub>2</sub><sup>−</sup> [18], BrO<sub>2</sub>F [19] or BrF<sub>4</sub>O<sup>−</sup> [6]. The halogen-oxygen bond is, also in this case, particularly strong. It is even stronger than in the related Br(V) oxohalides BrO<sub>2</sub>F<sub>2</sub><sup>−</sup> [18], BrO<sub>2</sub>F [19] or BrF<sub>4</sub>O<sup>−</sup> [6] and in the Br(VII) BrO<sub>4</sub><sup>−</sup> oxoanion (0.039 Å at 298 K) [4, 20].

Finally, a comparison of the two investigated F<sub>3</sub>XO molecules shows a similar overall vibrational behaviour and bond characteristics. The X=O bonds present similar strengths, although the Cl=O bond appears to be slightly stronger, as reflected by its slightly higher vibrational energy (1222 cm<sup>−1</sup> in F<sub>3</sub>ClO and 995 cm<sup>−1</sup> in F<sub>3</sub>BrO) and the lower temperature dependence of its mean amplitude of vibration (cf. Tables 1 and 2). On the other hand, in both cases the axial X–F bonds are weaker than the equatorial one and are somewhat ionic, as discussed in detail for F<sub>3</sub>ClO in the precedent paragraphs.

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