



Review

Mean amplitudes of vibration of molecules and ions with interhalogen bonds and related species

Enrique J. Baran

Centro de Química Inorgánica (CEQUINOR, CONICET/UNLP), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, C.Correo 962, 1900 La Plata, Argentina

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ABSTRACT

Mean amplitudes of vibration of molecules and ions containing interhalogen bonds are reviewed and critically analyzed. The presented information comprises pure interhalogen compounds as well as oxohalides. Correlations between mean amplitude values and structural and bond properties are discussed. Comparisons with data of related – specially isoelectronic – species are also performed. Characteristic ranges for the mean amplitudes of vibration for halogen–halogen and halogen–oxygen bonds could be established. The presented and discussed results are also of central importance for the analysis and interpretation of electron diffraction studies.

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E-mail address: baran@quimica.unlp.edu.ar.

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1. Introduction

Mean amplitudes of vibration are very useful and valuable parameters for the analysis of molecular structures and their vibrational behavior. 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.

As it is known, a rigid polyatomic molecule of a given symmetry can be described in its equilibrium position by a certain number of parameters, e.g., bond distances and interbond angles. However, and as a consequence of the molecular vibrations, real molecules are not actually rigid and, thus, their equilibrium parameters cannot be directly observed.

In the analysis of experimental data obtained by modern physico-chemical techniques such as X-ray or electron-diffraction, and microwave or high-resolution vibrational (infrared and Raman) spectroscopy, it becomes increasingly important to distinguish between the equilibrium interbond distances and various types of average distances.

The mean amplitudes of vibration are particularly useful in a work of this type and they are usually defined as the root-mean-square values according to [1]:

$$u_{ij} = \langle (R_{ij} - R_{ij}^e)^2 \rangle^{1/2} \quad (1)$$

which may be regarded as parameters of a non-rigid molecular model. In Eq. (1) *ij* refers to an arbitrary (bonded or non-bonded) atom pair. *R_{ij}* is the instantaneous interbond distance, and *R_{ij}^e* is the corresponding equilibrium distance and the mean value being a part of the definition (1) involves the statistical-mechanical middle. Consequently, mean amplitudes of vibration are temperature-dependent properties.

As mentioned above, the intensive study of mean amplitudes was initiated by the needs of modern electron-diffraction experiments, but they also proved to be of great interest in vibrational-spectroscopic studies independently. In fact, under the approximation of small harmonic vibrations, a mean-square amplitude matrix Σ has been devised, and shown to be equivalent to the well-known force-constant matrix, **F**. The matrix Σ is temperature-dependent and closely connected to the squared values of *u_{ij}*, as defined in Eq. (1).

In spectroscopic studies a special importance of the mean amplitudes lays in the fact that they can be used in accurate determinations of molecular force fields, if they can be obtained from electron diffraction-data with sufficient accuracy. In this sense, the mean amplitudes play the same role as Coriolis coupling and centrifugal distortion constants and the frequency data obtained from the vibrational spectra of isotopic species [2] all of which are closely connected with the force field.

Finally, it is interesting to mention that, in a similar way as for vibrational frequencies and force constants, mean amplitudes of vibration can be very characteristic values for both, bonded and non-bonded atoms. This means that if the stretching force constant and the corresponding frequency for a given chemical bond in different molecules are nearly the same, this will also be true for the mean amplitude of vibration of this bond [1,3,4]. On the other hand, bond strengths, as measured by the force constants, are inversely related to the mean amplitude values, i.e., a stronger bond (higher force constant) implies a lower mean amplitude of vibration.

It is also possible to establish different relations between mean amplitudes of vibration, force constants and other molecular parameters [3–7]. Therefore, the knowledge of the mean amplitude values can often provide an interesting insight into some structural and bond peculiarities in complex molecules. For example, in systematic studies performed on the structural characteristics of XF₅Z species [8–13], the calculation of mean amplitudes of vibrations allowed to confirm some intrinsic peculiarities which were not always shown from the analysis of other bond and molecular parameters [14].

During the last thirty years we have calculated mean amplitudes of vibration for a large series of molecules and ions containing interhalogen and halogen–oxygen bonds and related species. Most of our calculations were performed with the “Method of the Characteristic Vibrations” developed by Müller et al. [15] (cf. also [4,16]), which has been shown to provide excellent results for a wide range of molecular systems of very different symmetries and bonding characteristics (cf. for example [17–27]).

In this review we present in an ordered and systematic way the results of our own calculations, together with those of other authors, to allow a complete picture on the mean amplitudes of vibration and connected bond characteristics of systems containing interhalogen bonds. We have also tried to establish systematic correlations between mean amplitude values and other bond peculiarities and to make useful comparisons with related molecular systems.

2. Some comments on the bonding characteristics of the reviewed systems

The VSEPR model [28–32], together with the concept of atomic orbital hybridization [28,33], are very useful for the prediction of molecular geometries of compounds of the main group elements. Both aspects are widely used in teaching and are profusely discussed in practically all textbooks of General and Inorganic Chemistry. Notwithstanding, the participation of atomic d orbitals in bond formation between elements of groups 14–18 of the Periodic System has been intensively debated in the last years [34–37] and it is now recognized that they are not as important as could

be suspected from their participation in the formation of hybrid orbitals. In spite of the fact that the primary function of the d orbitals, introduced in theoretical calculations, seems to be the polarization of p orbitals, it has also been suggested that the qualitative influence of d orbitals on the stabilization of the molecular structures and in bond contraction phenomena cannot be neglected [35].

However, a great number of molecules and ions that will be discussed in this review violate the Lewis octet rule, i.e., around the central atom one counts more than four electronic pairs. In this sense, these species are usually defined as “hypervalent” compounds [37–39]. An interesting way for the description of chemical bonding in such type of molecules, is the 3-center-4-electron (3c–4e) MO bonding model, initially proposed by Rundle and co-workers [40,41] and Pimentel [42], which has gained increased acceptance [38,43], although it does not provide a complete bonding description for all classes of hypervalent species [37]. In this model, one p orbital of the central atom can overlap with ligand bonding orbitals (either pure p orbitals or hybrids) to form the usual trio of 3-centered orbitals: bonding, non-bonding, and antibonding. Consequently, the four valence electrons fill the first two of these orbitals and a single bond (or bonding MO) is spread over the three centers. The bonding orbital will necessarily withdraw some electron density from the central atom, placing it on the ligands, giving the bond ionic as well as covalent character [41]. These 3c–4e bonds, often called semi-ionic bonds, require that the terminal atoms be more electronegative than the central atom, and that these bonds may be longer than normal electron pair bonds between the same elements, since there is only one bonding pair for the two bonds.

Different aspects related to this model shall be discussed and commented on the basis of the concrete examples discussed along this review.

3. Pure interhalogen compounds

Apart from the pure diatomic X_2 halogen molecules, the simplest group of interhalogen species is conformed by the six diatomic XY molecules. Besides, an important number of other neutral or charged (anionic or cationic) interhalogen species covering a wide range of structures and stoichiometries is also known.

3.1. Neutral molecules

3.1.1. XY Species

The six diatomic XY molecules (ClF, BrF, IF, BrCl, ICl and IBr) constitute the simplest group of interhalogen molecules. In these cases the calculation of bond properties is very easy, as diatomic molecules only present one normal vibrational mode. From this unique mode one can estimate the force constant simply by the so-called “two-masses model” [44], whereas the mean amplitudes of vibration can be calculated by a method proposed by Kimura and Kimura, which is specially useful in cases of only one characteristic vibrational frequency [45], i.e.:

$$u_{XY}^2 = G_{XY} \cdot \Delta_1 \quad (2)$$

$$G_{XY} = \mu_X + \mu_Y \quad (2a)$$

$$\Delta_1 = \left[\frac{h}{8\pi^2 \nu_1} \right] \coth \left(\frac{h\nu_1}{2kT} \right) \quad (2b)$$

(μ_X and μ_Y are the reduced masses of the atoms X and Y and ν_1 is the characteristic vibrational frequency of the X–Y bond, in cm^{-1}).

Table 1

Mean amplitudes of vibration (in Å) and force constants (in $\text{mdyn}/\text{Å}$) for the diatomic XY interhalogen molecules [46]

T (K)	ClF	BrF	IF	BrCl	ICl	IBr
0	0.0420	0.0405	0.0409	0.0395	0.0399	0.0359
100	0.0420	0.0405	0.0409	0.0396	0.0401	0.0367
200	0.0421	0.0408	0.0414	0.0412	0.0425	0.0416
300	0.0430	0.0421	0.0431	0.0446	0.0469	0.0477
400	0.0446	0.0443	0.0457	0.0486	0.0517	0.0537
500	0.0468	0.0468	0.0487	0.0528	0.0564	0.0593
600	0.0491	0.0495	0.0518	0.0568	0.0610	0.0645
700	0.0516	0.0523	0.0548	0.0607	0.0653	0.0694
800	0.0541	0.0551	0.0579	0.0644	0.0694	0.0739
900	0.0566	0.0578	0.0608	0.0679	0.0733	0.0783
1000	0.0590	0.0604	0.0637	0.0714	0.0771	0.0824
f_{XY}	4.36	4.07	3.62	2.80	2.38	2.06

The mean amplitudes of vibration calculated with this procedure [46] in the temperature range, between 0 and 1000 K, are shown in Table 1 together with the values of the respective force constants, calculated in the form mentioned above.

From the values presented in Table 1 one can observe a somewhat unexpected behavior, as at the lowest temperatures the compounds with smaller force constants, present the lower mean amplitude values. Only at higher temperatures these relations become normal, in that compounds with the highest force constants, i.e., with stronger bonds, present lower mean amplitudes of vibration. This behavior constitutes a good example of the so-called “low temperature anomalies” of mean amplitude values. Such anomalies become always evident when the vibrations are dominated by mass effects rather than by the force-constant effects [47,48].

In such cases, at low temperatures, the higher masses of the vibrating units generate lower mean amplitude values practically as a consequence of their weights. At increasing temperatures, the mean amplitudes of vibration are mainly dominated by the bond strengths and the mass effects become negligible or can practically be neglected. This fact is also well known from the theory of molecular vibrations, and most concretely from the classical limit of the mean-square amplitude matrix Σ , which is only dependent of the respective force constant [1,47].

There is an additional interesting possibility to analyze the behavior of systems such as those presented in this section. It is possible to establish the following relation between mean amplitudes and force constants [4,7]:

$$u_{XY}^2 = \frac{kT}{f_{XY}} + \left[\frac{h}{64\pi^2 kT} \right] (\mu_X + \mu_Y) \quad (3)$$

From this expression it is easy to verify that at low temperatures the second term dominates the u -value, whereas the first term becomes increasingly preponderant with increasing temperatures, finally constituting the dominant factor.

3.1.2. X_2 Dihalogen molecules

A brief information on the mean amplitudes of vibration of the pure halogen molecules is presented here in order to allow some comparisons with the results of the previous section, and with the data presented in other sections of this review.

Mean amplitudes of vibration for chlorine, bromine and iodine have been investigated quite extensively by gaseous electron diffraction and also by calculations from spectroscopic data, including values from isotopic data [1]. Recently, we have performed a calculation of the mean amplitude values of the four diatomic halogen molecules using the same procedure outlined in

Table 2

Mean amplitudes of vibration (in Å) and force constants (in mdyn/Å) for the four halogen molecules [49]

T (K)	F ₂	Cl ₂	Br ₂	I ₂
0	0.0446	0.0413	0.0365	0.0358
100	0.0446	0.0413	0.0369	0.0377
200	0.0446	0.0420	0.0404	0.0451
298.16	0.0452	0.0442	0.0455	0.0527
300	0.0452	0.0442	0.0455	0.0529
400	0.0464	0.0472	0.0508	0.0601
500	0.0482	0.0506	0.0558	0.0666
600	0.0502	0.0540	0.0606	0.0727
700	0.0524	0.0574	0.0650	0.0782
800	0.0547	0.0606	0.0692	0.0835
900	0.0570	0.0638	0.0733	0.0886
1000	0.0593	0.0669	0.0771	0.0931
<i>f_{xx}</i>	4.46	3.25	2.36	1.60

the case of the XY molecules [45]. The results, in the temperature range between 0 and 1000 K, together with the respective bond force constants (calculated also, as above [44]) are shown in Table 2 [49].

Also for these simple diatomic molecules the mentioned “low temperature anomalies” are evident. Only at temperatures above 400 K a normal behavior can be observed for all the molecules. Besides, and although the force constant of F₂ is slightly higher than that of ClF, the mean amplitudes of vibration of the fluorine molecule are somewhat higher in the full temperature range. This behavior can surely be related to the great differences in bonding energy between both molecules (37.0 kcal/mol for F₂ and 59.5 kcal/mol for ClF [49]). In general, comparisons of this type, between halogen and interhalogen molecules, show a good correlation between the amplitude and bond energy values [49].

3.1.3. XF₃ Species

Chlorine and bromine trifluoride are two of the best known and well-characterized interhalogen compounds, whereas the corresponding iodine compound is relatively unstable, decomposing to I₂ and IF₃ above –20 °C [50]. The three species have a T-shaped structure of C_{2v} symmetry, consistent with the presence of ten electrons in the valence shell (formally a sp³d hybrid orbital) of the central atom. The values calculated for the mean amplitudes of vibration for the three molecules, at 0 and 298.16 K, are shown in Table 3 [17,51].

The most interesting trend derived from the comparison of the presented data is the fact that the X–F equatorial bond suffers a slight reinforcement on going from the ClF₃ to IF₃, confirming the general trend expected for bonding forces in this type of molecules, i.e., a reinforcement of the interhalogen bond with increasing difference in electronegativity of the involved atoms [28]. A similar trend cannot be observed for the axial bonds, although the three values are comparable and the IF₃ amplitude is intermediate between those of the other two molecules.

Table 3

Mean amplitudes of vibration (in Å) for the three XF₃ molecules at 0 and 298.16 K

Molecule	T (K)	<i>u</i> _{X–F(ax)}	<i>u</i> _{X–F(eq)}	<i>u</i> _{F(ax)–F(ax)}	<i>u</i> _{F(ax)–F(eq)}	Reference
ClF ₃	0	0.0476	0.0425	0.066	0.060	[17]
	298.16	0.0505	0.0473	0.077	0.067	
BrF ₃	0	0.0442	0.0407	0.070	0.063	[17]
	298.16	0.0473	0.0424	0.086	0.072	
IF ₃	0	0.0448	0.0401	0.057	0.057	[51]
	298.16	0.0489	0.0420	0.061	0.068	

Table 4

Mean amplitudes of vibration (in Å) for the three XF₅ molecules at 0 and 298.16 K [52]

Molecule	T (K)	<i>u</i> _{X–F(ax)}	<i>u</i> _{X–F(eq)}	<i>u</i> _{F(eq)F(eq)} short	<i>u</i> _{F(eq)F(eq)} long	<i>u</i> _{F(eq)F(ax)}
ClF ₅	0	0.0445	0.0474	0.0686	0.0588	0.0620
	298.16	0.0462	0.0507	0.0824	0.0640	0.0695
BrF ₅	0	0.0404	0.0427	0.0722	0.0560	0.0634
	298.16	0.0422	0.0452	0.0926	0.0598	0.0728
IF ₅	0	0.0380	0.0408	0.0764	0.0558	0.0660
	298.16	0.0394	0.0430	0.1052	0.0600	0.0785

Besides, the difference in the strength of the two types of bonds can also be related to the bonding peculiarities of these molecules. The equatorial X–F bond is a normal localized 2c–2e bonds, involving sp² hybrid orbitals of the central atoms (the two remaining lobes of this hybrids are occupied by the lone pairs). The two axial F atoms must then be in 3c–4e bonds, involving the third p atomic orbital of the central atoms.

3.1.4. XF₅ Species

This group of interhalogen molecules is also well known. They present a tetragonal pyramidal structure with C_{4v} symmetry. Their mean amplitudes of vibration were firstly calculated by Cyvin et al. [52] and recalculated some years later, with comparable results [53]. The obtained values are presented in Table 4.

As it can be seen, in all cases the mean amplitude values of the equatorial X–F bonds are higher than those of the respective axial bonds, indicating that the later are the strongest bonds. These results are in agreement with the bonding characteristics of these species in which the axial bonds may be described as normal single covalent bonds, whereas the equatorial ones can be described, essentially, as 3c–4e bonds (cf. also results for the related isoelectronic XF₅[–] (X = S, Se, Te) species [53,54].

Table 5

Mean amplitudes of vibration (in Å) for IF₇ at some selected temperatures, and comparison with values of the isoelectronic species TeF₇[–] and XeF₇⁺ [24]

T (K)	<i>u</i> _{I–F(eq)}	<i>u</i> _{I–F(ax)}	<i>u</i> _{F(eq)F(eq)/sh}	<i>u</i> _{F(eq)F(eq)/lg}	<i>u</i> _{F(ax)F(ax)}	
IF ₇	0	0.0408	0.0378	0.057	0.054	0.051
	298.16	0.0430	0.0390	0.062	0.056	0.053
	400	0.0456	0.0408	0.066	0.060	0.056
	600	0.0516	0.0454	0.076	0.068	0.063
	800	0.0577	0.0503	0.086	0.076	0.069
	1000	0.0634	0.0550	0.095	0.083	0.076
	TeF ₇ [–]	0	0.0423	0.0389	0.065	0.056
298.16		0.0452	0.0393	0.074	0.061	0.055
400		0.0482	0.0426	0.082	0.065	0.058
600		0.0550	0.0477	0.096	0.075	0.066
800		0.0617	0.0530	0.109	0.084	0.073
1000		0.0681	0.0582	0.121	0.092	0.080
XeF ₇ ⁺		0	0.0405	0.0374	0.060	0.055
	298.16	0.0427	0.0385	0.067	0.058	0.053
	400	0.0452	0.0403	0.073	0.062	0.057
	600	0.0511	0.0447	0.084	0.070	0.062
	800	0.0571	0.0494	0.096	0.079	0.069
	1000	0.0628	0.0540	0.106	0.087	0.076

sh: short distance; lg: long distance.

3.1.5. IF₇

Iodine heptafluoride is one of the most investigated interhalogen molecules from the structural, spectroscopic and theoretical points of view and it is so far the most-studied prototype for heptacoordination [55,56].

Mean amplitudes of vibration of IF₇ at room temperature were firstly calculated by Ramaswamy and Muthusubramanian [57] and later by Christe et al. [55]. A more complete calculation in the temperature range between 0 and 1000 K was performed later [24], using the most recently revised set of spectroscopic data [55]. Results of this calculation, at some selected temperatures are presented in Table 5.

From these results it is clearly evident that the axial bonds are appreciably stronger than the equatorial ones and present a lower temperature dependence. This fact is also reflected in the corresponding force constants for these two bonds ($f_{\text{I-F(ax)}} = 5.005$, $f_{\text{I-F(eq)}} = 3.947$ mdyn/Å [55]) and is in excellent agreement with the bond peculiarities of the molecule which can be explained on the basis of a simple model derived from XeF₄ [40–42,55]. The bonding in this square planar molecule can be described by two semi-ionic 3-center 4-electron (3c–4e) bonds for the four Xe–F bonds and two lone electron pairs on the central atom involving the sp_z hybrid orbital. The 3c–4e bonds involve the two remaining p orbitals (p_x and p_y) of xenon. Addition of an F[−] anion to the molecular plane results in pentagonal-planar XeF₅[−] and the formation of a semi-ionic 6-center 10-electrons (6c–10e) bond. The equatorial plane of IF₇ has essentially the same bonding as XeF₅[−] [55]. On the other hand, the two axial I–F bonds originated in normal two-electron bonds, are essentially covalent and, hence, shorter and stronger than the equatorial ones.

It is also interesting to compare the mean amplitudes of vibration of IF₇ with those of the isoelectronic and isostructural TeF₇[−] and XeF₇⁺ species. The heptafluorotellurate(VI) anion was identified in 1957 but was only characterized in detail more than thirty years later [58]. Simultaneously, and on the basis of electronic structure calculations using *ab initio* MO and density functional theories it has also been demonstrated that the XeF₇⁺ cation could also be a stable species belonging to the same structure. Mean amplitudes of vibration for these two ionic species are also included in Table 5.

As expected, also in these ions the mean amplitudes of vibration of the equatorial bonds show higher values than the respective axial bonds. On the other hand, the comparison of the three species included in Table 5 shows the expected trend for a series of this type in that the mean amplitudes of vibration of both types of X–F bonds diminish with increasing charge of the central atom, i.e., XeF₇⁺ < IF₇ < TeF₇[−], reflecting the expected bond strengthening. Besides, TeF₇[−] amplitudes show the greatest temperature dependence, a behavior which is also consistent with its weaker bonds [24,26]. Specially interesting are the relatively low mean amplitude values calculated for the axial Xe–F bonds in the XeF₇⁺ cation, which reflects the presence of a relatively strong linkage and presents the lowest value so far found in any xenon–fluorine species [24].

Finally, it is also worth mentioning that the SbF₇^{2−} and BiF₇^{2−} anions represent two additional examples of species structurally related to IF₇ [59]. Their mean amplitudes of vibration were also calculated and showed the expected behavior in comparison with the other species discussed in this section [60]. As SbF₇^{2−} is isoelectronic with TeF₇[−] and IF₇, it can also be included in the previously discussed series. As expected, the mean amplitudes of vibration for the Sb–F bonds are even higher than those of TeF₇[−] (for example, at 298.16 K: $u_{\text{Sb-F(eq)}} = 0.0497$ Å and $u_{\text{Sb-F(ax)}} = 0.0431$ Å) [60].

Table 6

Mean amplitudes of vibration (in Å) for XY₂⁺ species, at some selected temperatures, and force constants (mdyn/Å) for the respective X–Y bonds [61]

T (K)	ClF ₂ ⁺		BrF ₂ ⁺		ICl ₂ ⁺	
	$u_{\text{Cl-F}}$	$u_{\text{F...F}}$	$u_{\text{Br-F}}$	$u_{\text{F...F}}$	$u_{\text{I-Cl}}$	$u_{\text{Cl...Cl}}$
0	0.0408	0.061	0.0395	0.062	0.0406	0.069
298.16	0.0416	0.069	0.0409	0.072	0.0482	0.111
400	0.0430	0.075	0.0428	0.078	0.0533	0.127
600	0.0470	0.088	0.0476	0.092	0.0630	0.154
800	0.0515	0.099	0.0528	0.104	0.0717	0.178
1000	0.0561	0.110	0.0578	0.115	0.0797	0.198
$f_{\text{X-Y}}$	4.74		4.60		2.15	

3.2. Interhalogen cations

3.2.1. XY₂⁺ Species

Only a limited number of calculations have so far been performed for species of this type. They are restricted to the ClF₂⁺, BrF₂⁺ and ICl₂⁺ cations [61]. Results at some selected temperatures are shown in Table 6. The obtained values are relatively low, and are only comparable to those of the simple diatomic species ClF, BrF and IF (cf. Table 1), suggesting also in these cases relatively strong interhalogen bonds.

A comparison of the respective force constants shows that ICl₂⁺ presents the lowest value. Therefore, it is expected that this species presents the highest mean amplitudes of vibration in the full temperature range. Notwithstanding, it can be immediately seen that this does not occur at the lowest temperatures. Besides, also the comparison of the two fluoro-cations shows that BrF₂⁺ presents only above 400 K higher amplitude values than ClF₂⁺. These behaviors are again a manifestation of the so-called “low temperature anomalies”, discussed in detail in Section 3.1.1.

3.2.2. XF₄⁺ Species

These cations possess C_{2v} symmetry and their structures can be formally derived from a sp³d hybridization of the central atom. Therefore, there are two equatorially and two axially bonded fluorine atoms and a lone pair of electrons occupying the remaining equatorial position and the axial bonds are somewhat longer than the equatorial ones [62]. This is in agreement with the bonding schema that can be formulated for these species which is similar to that discussed for the XF₃ molecules (Section 3.1.3) but with only one electronic lone pair. As a consequence, the equatorial F atoms are attached to the central atom by normal localized two-electron bonds

Table 7

Mean amplitudes of vibration (in Å) for XF₄⁺ species, at three selected temperatures [62]

T (K)/ClF ₄ ⁺	$u_{\text{Cl-F(ax)}}$	$u_{\text{Cl-F(eq)}}$	$u_{\text{F(ax)F(ax)}}$	$u_{\text{F(eq)F(eq)}}$	$u_{\text{F(ax)F(eq)}}$
0	0.0440	0.0409	0.056	0.054	0.059
298.16	0.0458	0.0417	0.059	0.058	0.065
500	0.0507	0.0450	0.068	0.066	0.077
T (K)/BrF ₄ ⁺	$u_{\text{Br-F(ax)}}$	$u_{\text{Br-F(eq)}}$	$u_{\text{F(ax)F(ax)}}$	$u_{\text{F(eq)F(eq)}}$	$u_{\text{F(ax)F(eq)}}$
0	0.0408	0.0388	0.054	0.058	0.062
298.16	0.0426	0.0399	0.058	0.065	0.071
500	0.0476	0.0439	0.065	0.076	0.084
T (K)/IF ₄ ⁺	$u_{\text{I-F(ax)}}$	$u_{\text{I-F(eq)}}$	$u_{\text{F(ax)F(ax)}}$	$u_{\text{F(eq)F(eq)}}$	$u_{\text{F(ax)F(eq)}}$
0	0.0402	0.0378	0.052	0.058	0.065
298.16	0.0421	0.0391	0.057	0.065	0.077
500	0.0473	0.0431	0.065	0.076	0.092

Table 8

Mean amplitudes of vibration (in Å) of ClF_6^+ [65], BrF_6^+ [67] and IF_6^+ [66] at some selected temperatures

T (K)/ ClF_6^+	$u_{\text{Cl-F}}$	$u_{\text{FF/sh}}$	$u_{\text{FF/lg}}$
0	0.0415	0.058	0.052
300	0.0426	0.064	0.055
500	0.0463	0.074	0.061
T (K)/ BrF_6^+	$u_{\text{Br-F}}$	$u_{\text{FF/sh}}$	$u_{\text{FF/lg}}$
0	0.0392	0.062	0.052
300	0.0405	0.072	0.054
500	0.0446	0.085	0.060
T (K)/ IF_6^+	$u_{\text{I-F}}$	$u_{\text{FF/sh}}$	$u_{\text{FF/lg}}$
0	0.0367	0.066	0.049
300	0.0377	0.081	0.051
500	0.0412	0.098	0.056

sh: short distance; lg: long distance.

and the lone pair occupying the remaining equatorial position whereas the axial atoms are again in 3c–4e bonds.

The vibrational spectra of the three cations have been reported by Christe and Sawodny [63] and some of the deformational modes have been further reassigned [62]. Mean amplitudes of vibration for these species are shown in Table 7. As expected from the above discussion, the amplitude values of the axial bonds are always larger than those corresponding to the equatorial bonds. On the other hand, the amplitude values for the bonded atoms decrease from ClF_4^+ to BrF_4^+ and then remains practically constants to IF_4^+ . Interestingly, a similar trend is also observed in the isoelectronic SF_4 , SeF_4 and TeF_4 molecules [22].

A comparison of pairs of isoelectronic species shows the expected bond reinforcement in the case of the interhalogen cations, although this trend becomes only clearly evident in the case of the respective axial bonds, which amplitude values are appreciably lower for the cations. In the case of the equatorial bonds comparable values are found [22,62].

3.2.3. XF_6^+ Species

The three octahedral XF_6^+ species are known and well-characterized [64] and its mean amplitudes of vibration have been calculated and discussed many years ago [65–67]. Results of these calculations are presented in Table 8. As can be seen the mean amplitude values decreases from the chlorine to the iodine cation, indicating a steady increase of the bond strength in this direction, a reinforcement which can be clearly related to the differences in electronegativity between the component halogens [28].

On the other hand, these species present some of the lowest mean amplitude values determined for halogen–fluoride species, indicating that this Cl–F, Br–F and I–F bonds are among the strongest known interhalogen bonds.

Some comparisons with isoelectronic species are also interesting in this case. One remarkable aspect is that both ClF_6^+ and BrF_6^+ show practically the same mean amplitudes of vibration than the isoelectronic neutral SF_6 and SeF_6 molecules [18] whereas only IF_6^+ shows the expected trend, presenting slightly lower mean amplitudes than TeF_6 [18]. This fact indicates that also the chalcogen–fluorine bonds in the hexafluorides of these elements are particularly strong.

An extension of these comparisons to a wider group of species clearly confirms the expected trends, i.e., a diminution of the mean amplitude values with increasing charge of the central atom, as shown by the following values obtained at room temperature:

Table 9

Mean amplitudes of vibration (in Å) of ClF_2^- , BrF_2^- and IF_2^- , at some selected temperatures [71]

T (K)	ClF_2^-		BrF_2^-		IF_2^-	
	$u_{\text{Cl-F}}$	$u_{\text{F...F}}$	$u_{\text{Br-F}}$	$u_{\text{F...F}}$	$u_{\text{I-F}}$	$u_{\text{F...F}}$
0	0.0537	0.061	0.0492	0.062	0.0495	0.063
298.16	0.0595	0.067	0.0550	0.069	0.0566	0.071
400	0.0647	0.073	0.0599	0.075	0.0621	0.077
600	0.0751	0.085	0.0698	0.088	0.0729	0.090
800	0.0849	0.096	0.0791	0.099	0.0828	0.102
1000	0.0940	0.106	0.0876	0.110	0.0918	0.113

GaF_6^{3-} : 0.055 Å [68]; GeF_6^{2-} : 0.048 Å [69]; AsF_6^- : 0.043 Å [69]; SeF_6 : 0.040 Å [18]; BrF_6^+ : 0.041 Å.
 InF_6^{3-} : 0.055 Å [68]; SnF_6^{2-} : 0.047 Å [69]; SbF_6^- : 0.042 Å [69]; TeF_6 : 0.039 Å [18]; IF_6^+ : 0.038 Å.

3.3. Interhalogen anions

3.3.1. XY_2^- Species

A great number of species of this type is known [70], but mean amplitudes of vibration were calculated only for a limited number of them. The available data include the three fluorine containing anions [71] as well as BrCl_2^- , ICl_2^- and IBr_2^- [72]. Results are presented in Tables 9 and 10.

As it can be seen all these interhalogen bonds present very high mean amplitude values and an important temperature dependence. This behavior is typical for very weak bonds and for bonds which present important ionic contributions. In fact, all these XY_2 bonds can be described as semi-ionic 3c–4e bonds. The mentioned bond weakness is more notable in the case of the non-fluorine containing anions.

Interestingly, the values presented in Table 9 show that at room temperature the Cl–F bond is substantially weaker than the other two ones whereas the Br–F and I–F bonds are of similar strengths. This trend does not follow that of the respective stretching force constants ($f_r(\text{BrF}_2^-) > f_r(\text{ClF}_2^-) > f_r(\text{IF}_2^-)$ [73]), suggesting an additional mass effect which influences the mean amplitude values, as supported by the fact that with increasing temperatures the I–F bond becomes weaker than the Br–F bond [71].

Also in the case of the other three anions the mean amplitudes of vibration does not follow exactly the force constants trend. In this case, and although differences between them are very small, $f_r(\text{BrCl}_2^-) > f_r(\text{ICl}_2^-) > f_r(\text{IBr}_2^-)$ [74], on the basis of the amplitude values I–Cl is the strongest whereas Br–Cl is the weakest bond.

Finally, a comparison of the mean amplitude values for the isoelectronic pairs $\text{BrF}_2^-/\text{KrF}_2$ and $\text{IF}_2^-/\text{XeF}_2$ [71] shows the expected bond reinforcement on going from the anions to the neutral molecules, confirming also that the effect of semi-ionic bonds is less important in the second case [71,73].

Table 10

Mean amplitudes of vibration (in Å) of BrCl_2^- , ICl_2^- and IBr_2^- , at some selected temperatures [72]

T (K)	BrCl_2^-		ICl_2^-		IBr_2^-	
	$u_{\text{Br-Cl}}$	$u_{\text{Cl...Cl}}$	$u_{\text{I-Cl}}$	$u_{\text{Cl...Cl}}$	$u_{\text{I-Br}}$	$u_{\text{Br...Br}}$
0	0.0539	0.060	0.0507	0.061	0.0453	0.051
298.16	0.0752	0.079	0.0708	0.083	0.0732	0.085
400	0.0853	0.089	0.0803	0.093	0.0838	0.097
600	0.1029	0.107	0.0968	0.113	0.1018	0.118
800	0.1181	0.123	0.1111	0.129	0.1172	0.136
1000	0.1317	0.137	0.1239	0.144	0.1309	0.152

Table 11
Mean amplitudes of vibration (in Å) for XY_4^- anions at 0 and 298.16 K

Anion	T (K)	u_{X-Y}	$u_{F...F/sh}$	$u_{F...F/lg}$	Reference
ClF_4^-	0	0.0513	0.079	0.062	[75]
	298.16	0.0560	0.104	0.069	
BrF_4^-	0	0.0477	0.082	0.060	[75]
	298.16	0.0526	0.115	0.067	
IF_4^-	0	0.0467	0.089	0.060	[75]
	298.16	0.0520	0.139	0.066	
ICl_4^-	0	0.0480	0.074	0.059	[76]
	298.16	0.0639	0.123	0.078	

sh: short distance; lg: long distance.

Table 12
Mean amplitudes of vibration (in Å) for ClF_6^- and BrF_6^- at 0 and 298.16 K

Anion	T (K)	u_{X-Y}	$u_{F...F/sh}$	$u_{F...F/lg}$	Reference
ClF_6^-	0	0.0514	0.078	0.067	[80]
	298.16	0.0572	0.102	0.077	
BrF_6^-	0	0.0458	0.082	0.061	[80]
	298.16	0.0498	0.115	0.067	

sh: short distance; lg: long distance

3.3.2. XY_4^- Species

Mean amplitudes of vibration have been calculated for the three tetrafluoro anions [75] as well as for ICl_4^- [76]. Results, at the temperatures of 0 and 298.16 K, are presented in Table 11.

The mean amplitude values for the XF_4^- species are comparable, but somewhat smaller to those calculated for the corresponding XF_2^- anions in agreement with the similar bonding characteristics of both series. Similarly as for the even discussed XF_2^- species, the values for the X–F bonds decreases from ClF_4^- to BrF_4^- and then remain practically constant on going to IF_4^- . Notwithstanding, in this case the behavior is in agreement with the variation of the respective force constants ($f_r(ClF_4^-) < f_r(BrF_4^-) \cong f_r(IF_4^-)$ [77]).

The ICl_4^- values are also slightly lower than those of ICl_2^- but appreciably higher than those of IF_4^- .

Also in this case the isoelectronic pair IF_4^-/XeF_4 shows the expected trend as the molecule shows a larger Xe–F force constant and a smaller mean amplitude value (0.046 Å at 298 K) [78].

3.3.3. XF_6^- Species and the IF_8^- anion

The synthesis and general characterization of the three XF_6^- anions have been reported some years ago but only very recently complete vibrational-spectroscopic information for the two octahedral species ClF_6^- and BrF_6^- become available [79]. On the basis of these data we have now performed a first estimation of its mean amplitude values [80], which are presented in Table 12. The values obtained for the respective X–F bonds lie, as expected, appreciably higher than in the corresponding XF_5^- and XF_4^+ species.

Besides, also for the interesting IF_8^- anion (D_{4d} symmetry) a complete assignment of the vibrational spectra, supported by

Table 13
Mean amplitudes of vibration (in Å) for IF_8^- at some selected temperatures [80]

T (K)	u_{I-F}	$u_{F...F}$
0	0.0426	0.061
100	0.0426	0.061
200	0.0433	0.063
298.16	0.0455	0.068
300	0.0455	0.068
400	0.0486	0.074

Table 14
Mean amplitudes of vibration (in Å) of IF_5^{2-} [83] and XeF_5^- [84] at some selected temperatures

IF_5^{2-}/T (K)	u_{I-F}	$u_{F...F}$ (in-plane)	$u_{F...F}$ (out-of-plane)
0	0.0511	0.079	0.061
298.16	0.0602	0.105	0.068
400	0.0665	0.118	0.073
600	0.0784	0.142	0.085
800	0.0892	0.162	0.096
1000	0.0991	0.181	0.107
XeF_5^-/T (K)	u_{Xe-F}	$u_{F...F}$ (in-plane)	$u_{F...F}$ (out-of-plane)
0	0.0464	0.069	0.059
298.16	0.0515	0.083	0.065
400	0.0559	0.092	0.070
600	0.0649	0.109	0.081
800	0.0733	0.124	0.091
1000	0.0812	0.138	0.101

theoretical calculations, was recently published [79], allowing also an estimation of its mean amplitudes of vibration [80] which are presented in Table 13. The values obtained for the I–F bond are only somewhat higher than that calculated for the equatorial I–F bond in IF_7^- but appreciably higher than that determined for IF_6^+ .

3.3.4. IF_5^{2-}

The first example of a chemical species adopting the unusual pentagonal-planar geometry was the XeF_5^- anion, characterized in 1991 [81], and some years later the isoelectronic IF_5^{2-} was also reported [82] and its mean amplitudes of vibration calculated [83]. The results of these calculations are shown in Table 14.

The results indicate that IF_5^{2-} presents a similar behavior than XeF_5^- , which mean amplitudes of vibration are also known [84] and are also included in Table 14. Notwithstanding, and as expected, the values for the I–F bonds are appreciably higher than those calculated for the Xe–F bonds, in agreement with the additional negative charge present over the iodine species and its lower nuclear charge. These two factors evidently produce an enhancement of the I–F bond polarity, generating a weakening of these bonds [82,83], which can also be visualized from the strong temperature dependence of its amplitude values, which in this case is yet more important than in XeF_5^- (cf. again Table 14).

However, the very strong temperature dependence for the non-bonded in-plane F...F distances suggests that the congestion effect on the molecular plane, admitted in the case of XeF_5^- [81,84] has a higher impact in the case of the IF_5^{2-} structure, contributing additionally to the I–F bond polarity and lengthening. It is also interesting to mention that the mean amplitudes of this anion are higher than those of IF_4^- (cf. Section 3.3.2), in which iodine presents the same nuclear charge, reflecting the impact of the addition of the fifth fluorine atom on bond weakening.

4. Oxohalides

An important number of neutral or ionic oxohalides of different stoichiometries is known and well characterized and mean amplitudes of vibration of most of them have been calculated.

4.1. Neutral molecules

4.1.1. $FClO$

Chlorosyl fluoride, $FClO$, is a very interesting molecule as it consists of a hypervalent chlorine atom bonded to the two most electronegative elements, fluorine and oxygen, in an angular, C_s -symmetry, arrangement. Its mean amplitudes of vibration were

Table 15
Mean amplitudes of vibration (in Å) of FClO, at some selected temperatures [85]

T (K)	$u_{\text{Cl-O}}$	$u_{\text{Cl-F}}$	$u_{\text{F...O}}$
0	0.0383	0.0476	0.057
298.16	0.0386	0.0504	0.068
400	0.0393	0.0535	0.075
600	0.0417	0.0607	0.088
800	0.0448	0.0679	0.100
1000	0.0482	0.0748	0.111

calculated [85] on the basis of recently reported high-resolution FTIR data [86]. Results, at some selected temperatures, are shown in Table 15.

The obtained results confirm the existence of a relatively strong Cl–O bond and a weaker Cl–F bond, reflected in higher mean amplitude values and in a stronger temperature dependence of this last bond. This behavior is also in agreement with the calculated force constants ($f(\text{Cl–O}) = 7.01 \text{ mdyn/Å}$, $f(\text{Cl–F}) = 2.51 \text{ mdyn/Å}$) [86]. A comparison with related species also shows that the F–Cl bond of this molecule presents intermediate values between the ClO_2F_2^- anion, which represents an extreme case in which the axial ClF_2 linkage can practically be described as pure semi-ionic 3c–4e bonds (cf. Section 4.3.1) and the strong covalent bonds present in ClF and ClF_2^+ , but supports the fact that it is evidently closer to a semi-ionic bond [85].

4.1.2. FXO_2 Species

Mean amplitudes of vibration for the pyramidal FClO_2 [87] and FBrO_2 [88] molecules were calculated more than thirty years ago. Results, at some selected temperatures, are shown in Table 16. From the presented data it becomes evident that both bonds are stronger in the chlorine species. Furthermore, the Br–F bond presents a more ionic character than the respective Cl–F linkage, showing also a more important temperature dependence.

4.1.3. FXO_3 Species

Mean amplitudes of vibration of FClO_3 have been calculated by different authors from spectroscopic data [15,89,90] and have also been experimentally determined by electron diffraction measurements [90]. Data for the respective bromine species are also known [91]. Results, at 0 and 298 K, are presented in Table 17.

4.1.4. F_3XO Species

For molecules of this stoichiometry mean amplitude values have been calculated for the respective chlorine species [92]. Their vibrational spectra are consistent with a trigonal bipyramidal structure around the central chlorine atom (C_3 -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

Table 16
Mean amplitudes of vibration (in Å) of FClO_2 [87] and FBrO_2 [88], at some selected temperatures

FClO_2/T (K)	$u_{\text{Cl-O}}$	$u_{\text{Cl-F}}$	$u_{\text{O...O}}$	$u_{\text{F...O}}$
0	0.0358	0.0464	0.054	0.061
298.16	0.0360	0.0487	0.056	0.069
400	0.0364	0.0515	0.059	0.075
600	0.0380	0.0580	0.067	0.087
FBrO_2/T (K)	$u_{\text{Br-O}}$	$u_{\text{Br-F}}$	$u_{\text{O...O}}$	$u_{\text{F...O}}$
0	0.0368	0.0465	0.060	0.068
298.16	0.0373	0.0508	0.067	0.082
400	0.0382	0.0548	0.072	0.091
600	0.0410	0.0632	0.083	0.107

Table 17
Mean amplitudes of vibration (in Å) of FClO_3 [89] and FBrO_3 [91] at 0 and 298 K

FClO_3/T (K)	$u_{\text{Cl-O}}$	$u_{\text{Cl-F}}$	$u_{\text{O...O}}$	$u_{\text{F...O}}$
0	0.0354	0.0431	0.053	0.053
298	0.0356	0.0446	0.056	0.065
FBrO_3/T (K)	$u_{\text{Br-O}}$	$u_{\text{Br-F}}$	$u_{\text{O...O}}$	$u_{\text{F...O}}$
0	0.037	0.043	0.059	0.069
298	0.045	0.037	0.066	0.084

[93]. This structural proposal was further confirmed by a gas electron diffraction study [94].

On the other hand, the analysis of the IR and Raman spectra of the related bromine compound, F_3BrO , suggests that, although it is not a monomeric species it possesses a similar structure as F_3ClO , presenting some kind of molecular association which apparently involves mainly the Br–F(axial) bonds [95]. Therefore, and on the basis of the so far available spectroscopic data, it was also possible to make an estimation of the mean amplitude values of the bromine compound [92].

Mean amplitudes of vibration of both molecules, at some selected temperatures, are shown in Table 18. As it can be seen, the halogen–oxygen bond is particularly strong, as reflected by the relatively low mean amplitude values and its weak temperature dependence. Besides, the values calculated for both types of X–F bonds reflect different behaviors, indicating that the equatorial bond is stronger than the two axial ones. This fact is supported by the structural characteristics of both molecules in which the axial F–X–F bonds may be described by a semi-ionic 3c–4e bond [92].

In the case of F_3ClO it is also interesting to make a comparison with the isoelectronic F_3SO^- anion [96]. As expected, the X=O bond presents somewhat higher mean amplitude values in the anion, over the full temperature range and the same behavior is found for the X–F bonds at room temperature (for example, at 298.16 K, $u_{\text{S-O}} = 0.0366 \text{ Å}$, $u_{\text{S-F(ax)}} = 0.0519 \text{ Å}$, $u_{\text{S-F(eq)}} = 0.0454 \text{ Å}$ [25]). This trend is not maintained in the case of the X–F (equatorial) bonds at higher temperature at which the S–F bond shows somewhat lower mean amplitude values (for example, at 400 K, $u_{\text{S-F(eq)}} = 0.0474 \text{ Å}$ [25]).

4.1.5. F_3IO

This iodine oxofluoride is the only known species of this type. A first structural analysis of this molecule was reported by Bartell et al., on the basis of a combined electron diffraction–microwave study [97]. They found that the I–F (axial) bonds are slightly longer than the respective I–F (equatorial) bonds. Using the geometrical parameters of this study, together with the spectroscopic data

Table 18
Mean amplitudes of vibration (in Å) of F_3ClO and F_3BrO [92], at some selected temperatures

$\text{F}_3\text{ClO}/T$ (K)	$u_{\text{Cl-O}}$	$u_{\text{Cl-F(eq)}}$	$u_{\text{Cl-F(ax)}}$	$u_{\text{F...O}}$	$u_{\text{F(ax)...F(eq)}}$
0	0.0357	0.0443	0.0477	0.046	0.061
298.16	0.0359	0.0459	0.0509	0.049	0.067
400	0.0363	0.0481	0.0542	0.052	0.073
600	0.0380	0.0536	0.0616	0.059	0.084
800	0.0403	0.0595	0.0691	0.066	0.095
1000	0.0430	0.0652	0.0760	0.072	0.105
$\text{F}_3\text{BrO}/T$ (K)	$u_{\text{Br-O}}$	$u_{\text{Br-F(eq)}}$	$u_{\text{Br-F(ax)}}$	$u_{\text{F...O}}$	$u_{\text{F(ax)...F(eq)}}$
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

Table 19
Mean amplitudes of vibration (in Å) of F₅IO at some selected temperatures [13]

T (K)	<i>u</i> _{I–O}	<i>u</i> _{I–F(eq)}	<i>u</i> _{I–F(ax)}	<i>u</i> _{F(eq)F(eq)}	<i>u</i> _{OF(eq)}	<i>u</i> _{F(eq)F(ax)}
0	0.0358	0.0383	0.0399	0.064	0.063	0.071
298.16	0.0362	0.0397	0.0418	0.075	0.073	0.091
400	0.0370	0.0416	0.0441	0.083	0.079	0.102
600	0.0399	0.0464	0.0497	0.097	0.092	0.121
800	0.0433	0.0515	0.0554	0.111	0.105	0.139
1000	0.0469	0.0564	0.0609	0.123	0.116	0.154

reported by Smith and Begun [98] a set of mean amplitudes of vibration for this molecule was calculated [13]. Despite the fact that the obtained values, presented in Table 19, show an excellent agreement with those obtained experimentally [97] they show some differences with those reported earlier [57], and calculated on the basis of the same spectroscopic data. The results of Table 19 clearly reflect the above mentioned structural peculiarity, i.e., $r(\text{I–F(ax)}) > r(\text{I–F(eq)})$, in that the mean amplitudes of vibration of the axial bond are higher than that of the equatorial bonds. A totally similar behavior was found for other ZXY₅ species, as discussed in Ref. [14].

On the other hand, it must be mentioned that an independent theoretical calculation for F₅IO, complemented by a force field and normal coordinate analysis and by comparison with related isoelectronic species, suggests that all the I–F bonds are of comparable lengths [99]. Notwithstanding, and although experimental structural data for the isoelectronic F₅TeO[–] anion also show practically the equivalence of all Te–F bond lengths [100], the force constants of the axial bonds are slightly lower than those of the equatorial ones [100,101] generating again higher mean amplitudes of vibration for the axial Te–F bond [102].

4.2. Oxohalogen cations

4.2.1. F₂XO⁺ Species

The pyramidal cations F₂ClO⁺ and F₂BrO⁺ are so far the only oxohalide cations for which mean amplitudes of vibration were calculated [103], on the basis of known spectroscopic data [104,105]. Results, at different temperatures, are shown in Table 20.

As it can be seen, the X–O bonds are particularly strong, as reflected by their relatively low mean amplitude values and weak temperature dependencies. A comparison with the values calculated for the related F₃XO oxides (cf. Section 4.1.4) shows a reinforcement of this bond in the present cases, in agreement with

Table 20
Mean amplitudes of vibration (in Å) of F₂ClO⁺ and F₂BrO⁺ at some selected temperatures [103]

F ₂ ClO ⁺ /T (K)	<i>u</i> _{Cl–F}	<i>u</i> _{Cl–O}	<i>u</i> _{F...F}	<i>u</i> _{F...O}
0	0.0436	0.0340	0.062	0.045
298.16	0.0450	0.0341	0.071	0.049
400	0.0471	0.0344	0.078	0.053
600	0.0523	0.0356	0.091	0.061
800	0.0579	0.0375	0.103	0.068
1000	0.0634	0.0397	0.114	0.075
F ₂ BrO ⁺ /T (K)	<i>u</i> _{Br–F}	<i>u</i> _{Br–O}	<i>u</i> _{F...F}	<i>u</i> _{F...O}
0	0.0413	0.0347	0.068	0.054
298.16	0.0432	0.0349	0.083	0.063
400	0.0456	0.0355	0.092	0.069
600	0.0514	0.0376	0.109	0.080
800	0.0573	0.0404	0.124	0.091
1000	0.0629	0.0434	0.138	0.101

Table 21
Mean amplitudes of vibration (in Å) of F₂ClO₂[–] [110], F₂BrO₂[–] [111] and F₂IO₂[–] [111] at some selected temperatures

F ₂ ClO ₂ [–] /T (K)	<i>u</i> _{Cl–O}	<i>u</i> _{Cl–F}	<i>u</i> _{O...O}	<i>u</i> _{F...F}	<i>u</i> _{F...O}
0	0.0364	0.0550	0.052	0.070	0.070
298.16	0.0366	0.0622	0.054	0.083	0.084
400	0.0370	0.0680	0.056	0.092	0.093
600	0.0389	0.0793	0.063	0.109	0.110
800	0.0414	0.0899	0.069	0.124	0.125
1000	0.0443	0.0996	0.075	0.138	0.139
F ₂ BrO ₂ [–] /T (K)	<i>u</i> _{Br–O}	<i>u</i> _{Br–F}	<i>u</i> _{O...O}	<i>u</i> _{F...F}	<i>u</i> _{F...O}
0	0.0375	0.0514	0.056	0.069	0.057
298.16	0.0380	0.0591	0.060	0.081	0.068
400	0.0390	0.0649	0.065	0.090	0.075
600	0.0421	0.0761	0.073	0.106	0.089
800	0.0458	0.0865	0.082	0.121	0.102
1000	0.0497	0.0959	0.090	0.134	0.113
F ₂ IO ₂ [–] /T (K)	<i>u</i> _{I–O}	<i>u</i> _{I–F}	<i>u</i> _{O...O}	<i>u</i> _{F...F}	<i>u</i> _{F...O}
0	0.0379	0.0476	0.059	0.061	0.062
298.16	0.0386	0.0534	0.066	0.068	0.073
400	0.0399	0.0582	0.071	0.073	0.081
600	0.0436	0.0678	0.082	0.085	0.095
800	0.0478	0.0768	0.092	0.096	0.108
1000	0.0520	0.0851	0.101	0.107	0.120

the presence of the positive charge. The mean amplitudes of vibration for the X–F bonds are slightly lower than those determined for the equatorial X–F in the related oxides, also pointing to a reinforcement of this bond on going from the molecule to the cation. Moreover, the X–O and X–F mean amplitude values for both cations are comparable to those calculated for the isoelectronic F₂SO and F₂SeO molecules [106].

All the commented results indicate that the bonding of these cationic species can be described, essentially, by a covalent bond model, involving sp³ hybridized central halogen atoms [103].

4.3. Oxohalogen anions

4.3.1. F₂XO₂[–] Species

The structure of these anions can be formally derived from an sp³d hybridization of the central X halogen atom, i.e., this atom is located at the center of a trigonal bipyramid, the two fluorine atoms at the apices and the oxygen atoms, together with a lone electronic pair, at the basis of the bipyramid. Vibrational spectra of the three species of this type are well-known [107–109]. On the basis of this information the mean amplitudes of vibration of these anions were calculated [110,111].

The obtained results are presented in Table 21. The values calculated for the X–O bonds confirm the existence of relatively strong halogen–oxygen bonds and, although their amplitude values are comparable at the lowest temperature, increasing differences in the order F₂ClO₂[–] < F₂BrO₂[–] < F₂IO₂[–] are observed at increasing temperatures. This order follows the decrease of electronegativity of the halogen atoms, showing a reinforcement of this bond that parallels the electronegativity of the halogen atom. A different trend is observed for the interhalogen bonds. In this case, bond reinforcement occurs in the same direction as the increase in electronegativity difference between the two halogen atoms, i.e., the I–F bond is the strongest whereas the Cl–F bond is the weakest one. The mean amplitude values for these bonds are between the highest so far calculated for these type of linkages. Values found in F₂ClO₂[–] and F₂BrO₂[–] are even higher as those calculated in the related XF₂[–] species (cf. Section 3.3.1). Evidently, in all these anions the presence of very strong halogen–oxygen

Table 22

Mean amplitudes of vibration (in Å) of the three F_4XO^- anions at some selected temperatures [114]

F_4ClO^-/T (K)	u_{Cl-O}	u_{Cl-F}	$u_{F...F}$ (short)	$u_{F...F}$ (long)	$u_{F...O}$
0	0.0356	0.0511	0.082	0.066	0.064
298.16	0.0358	0.0555	0.113	0.076	0.072
400	0.0361	0.0597	0.128	0.084	0.079
600	0.0377	0.0687	0.154	0.098	0.092
800	0.0400	0.0774	0.177	0.111	0.104
1000	0.0426	0.0854	0.197	0.124	0.116
F_4BrO^-/T (K)	u_{Br-O}	u_{Br-F}	$u_{F...F}$ (short)	$u_{F...F}$ (long)	$u_{F...O}$
0	0.0369	0.0474	0.083	0.062	0.065
298.16	0.0373	0.0521	0.118	0.069	0.074
400	0.0382	0.0564	0.134	0.076	0.080
600	0.0411	0.0653	0.161	0.088	0.094
800	0.0446	0.0737	0.185	0.100	0.107
1000	0.0482	0.0815	0.206	0.110	0.118
F_4IO^-/T (K)	u_{I-O}	u_{I-F}	$u_{F...F}$ (short)	$u_{F...F}$ (long)	$u_{F...O}$
0	0.0366	0.0456	0.087	0.059	0.065
298.16	0.0371	0.0501	0.133	0.064	0.075
400	0.0381	0.0542	0.151	0.069	0.082
600	0.0412	0.0627	0.183	0.080	0.096
800	0.0449	0.0708	0.210	0.090	0.109
1000	0.0487	0.0783	0.235	0.100	0.121

bonds contributes to the enhancement of the ionic character of the halogen–fluorine bonds and the two axial X–F bonds may be considered as semi-ionic 3c–4e bonds.

Finally, it is also interesting to make some comparisons between the isoelectronic $F_2IO_2^-/F_2XeO_2$ pair. As in other previously commented cases the mean amplitude values of the molecule are appreciable lower than those of the anion [112], clearly reflecting the expected bond reinforcement. Besides, the mean amplitudes of vibration of the non-bonded pairs present comparable values in both species although in the xenon compound $u_{F...F}$ values are slightly lower than $u_{O...O}$ values [112].

4.3.2. F_4XO^- Species

The mean amplitudes of vibration of the three tetrafluoroxyhalate(V) anions were calculated on the basis of the vibrational spectra and force field calculations reported by Christie et al. [113]. The results, at different temperatures, are presented in Table 22 [114]. The obtained value for these square pyramidal anions can be compared with those of the corresponding square planar XF_4^- anions (Section 3.3.2; Table 11). This comparison shows similar values for both series and also similar, and relatively important, temperature dependences, in good agreement with similar bonding characteristics of the X–F linkages in both anions. Besides, a good correlation can be established between the force constants [113] and the mean amplitude values for these bonds. The stepwise increase of force constants with increasing mass of the central atom, parallels the diminution of amplitude values in the same direction [114].

On the other hand, and due to the fact that these linkages present a partial ionic character, the corresponding X–O bonds attain an important reinforcement derived from the increment of positive charge on the central atom. This fact is reflected in the relatively low mean amplitude values of these bonds.

It is also here interesting to make a brief comparison of F_4IO^- with the isoelectronic F_4XeO [52]. As expected, in this last case the mean amplitudes of vibration of the Xe–F and Xe–O bonds are slightly lower than those of the I–F and I–O bonds in the anion.

Table 23

Mean amplitudes of vibration (in Å) of the isoelectronic anions $F_5IO_2^-$ and F_5XeO^- at some selected temperatures [117]

$F_5IO_2^-/T$ (K)	u_{I-O}	u_{I-F}	$u_{F...F}$ (short)	$u_{F...F}$ (long)	$u_{F...O}$
0	0.0373	0.0485	0.070	0.062	0.063
298.16	0.0379	0.0551	0.084	0.070	0.076
400	0.0390	0.0603	0.093	0.076	0.084
600	0.0424	0.0706	0.110	0.086	0.100
800	0.0464	0.0800	0.125	0.100	0.114
1000	0.0504	0.0887	0.139	0.111	0.126
F_5XeO^-/T (K)	u_{Xe-O}	u_{Xe-F}	$u_{F...F}$ (short)	$u_{F...F}$ (long)	$u_{F...O}$
0	0.0366	0.0460	0.066	0.060	0.059
298.16	0.0372	0.0509	0.078	0.066	0.070
400	0.0382	0.0552	0.085	0.072	0.077
600	0.0414	0.0640	0.100	0.083	0.090
800	0.0451	0.0724	0.115	0.094	0.102
1000	0.0490	0.0801	0.127	0.104	0.114

4.3.3. $F_5IO_2^-$ and F_6IO^-

These two anions belong to the interesting species formally derived from a sp^3d^3 hybridization of the central atom and are, therefore, structurally related to IF_7 . Moreover, they are isoelectronic with F_5XeO^- and $F_6TeO_2^-$, respectively.

Mean amplitudes of vibration for the $F_5IO_2^-/F_5XeO^-$ pair, were calculated on the basis of known spectroscopic and structural data [115,116] and results, at some selected temperatures, are shown in Table 23 [117]. A comparison of these values immediately shows that the I–O bonds are slightly weaker than the Xe–O bonds in the full temperature range, also in good agreement with the respective force constants ($f_r(I-O) = 6.01$ mdyn/Å < $f_r(Xe-O) = 6.33$ mdyn/Å [116]). The same trend is observed for the respective X–F bonds, in agreement with the general expectations for an isoelectronic pair of this type.

It can also be seen that the mean amplitude values for the X–O bonds lie in a very restricted range, reflecting relatively strong binding. For such species, with pentagonal-pyramidal geometry, this finding confirms that the negative charge is concentrated mainly on the fluorine atoms [55,56]. Besides, as seen also from Table 23 the X–F bonds show relatively high mean amplitudes of vibration, an observation that goes with the proposed bonding model for these species, which suggests a highly ionic 6-center 10-electron (6c–10e) bond for the five fluorine atoms, originated by the interaction of these atoms with a p_x , p_y hybrid orbital of the central atom [55,56,117]. In this scheme the axial oxygen ligand is covalently bonded to the central atom through a sp_2 hybrid orbital, supporting the higher strength of this bond.

Table 24

Mean amplitudes of vibration (in Å) of the isoelectronic anions F_6IO^- and $F_6TeO_2^-$ at some selected temperatures [120]

F_6IO^-/T (K)	u_{I-O}	$u_{I-F}(eq.)$	$u_{I-F}(ax.)$	$u_{F...F}$ (short)	$u_{F...F}$ (long)
0	0.0369	0.0418	0.0396	0.059	0.056
298.16	0.0375	0.0444	0.0414	0.064	0.058
400	0.0386	0.0475	0.0440	0.065	0.062
600	0.0419	0.0537	0.0491	0.080	0.072
800	0.0456	0.0600	0.0548	0.090	0.081
1000	0.0497	0.0663	0.0600	0.099	0.090
$F_6TeO_2^-/T$ (K)	u_{Te-O}	$u_{Te-F}(eq.)$	$u_{Te-F}(ax.)$	$u_{F...F}$ (short)	$u_{F...F}$ (long)
0	0.0379	0.0439	0.0407	0.063	0.059
298.16	0.0386	0.0475	0.0429	0.070	0.064
400	0.0399	0.0511	0.0455	0.076	0.069
600	0.0436	0.0587	0.0515	0.089	0.079
800	0.0477	0.0661	0.0575	0.101	0.089
1000	0.0519	0.0730	0.0632	0.112	0.099

Table 25

Mean amplitudes of vibration (in Å) of *trans*-F₄IO₂⁻ [123] and *trans*-F₅IO₂²⁻ [124], at some selected temperatures

F ₄ IO ₂ ⁻ /T (K)	u _{I-O}	u _{I-F}	u _{O...O}	u _{F...F}	u _{F...O}
0	0.0372	0.0421	0.051	0.077	0.055
298.16	0.0378	0.0448	0.052	0.106	0.063
400	0.0390	0.0478	0.053	0.119	0.069
600	0.0424	0.0544	0.058	0.143	0.081
800	0.0464	0.0610	0.064	0.164	0.091
1000	0.0504	0.0672	0.070	0.183	0.101
F ₅ IO ₂ ²⁻ /T (K)	u _{I-O}	u _{I-F}	u _{O...O}	u _{F...F}	u _{F...O}
0	0.0380	0.0455	0.052	0.078	0.060
298.16	0.0388	0.0499	0.053	0.103	0.071
400	0.0401	0.0541	0.055	0.115	0.079
600	0.0438	0.0625	0.060	0.138	0.093
800	0.0480	0.0705	0.066	0.158	0.105
1000	0.0523	0.0780	0.072	0.177	0.117

Mean amplitudes of vibration for the second isoelectronic pair, the pentagonal-bipyramidal anions F₆IO⁻/F₆TeO²⁻ [118,119], are presented in Table 24 [120]. In both cases, the mean amplitude values for the X–F equatorial bonds are somewhat higher than those corresponding to the respective axial bonds, confirming that the last ones are slightly stronger. This behavior is in agreement with the bonding model proposed for these species, which is analogous to that described above for the F₅IO²⁻/F₅XeO⁻ pair, involving semi-ionic equatorial X–F bonds. On the other hand, also in this case the general behavior expected for a pair of isoelectronic species is clearly fulfilled.

4.3.4. *trans*-F₄IO₂⁻ and *trans*-F₅IO₂²⁻

The synthesis of *cis* and *trans* mixtures of F₄IO₂⁻ was reported more than twenty years ago [121] whereas *trans*-F₅IO₂²⁻ constitutes a new recent example of heptacoordination [122]. The mean amplitudes of vibration calculated for these anions [123,124], at some selected temperatures, are presented in Table 25.

An analysis of the obtained results shows that in both cases that the I–O bonds are appreciable stronger than the I–F bonds, the former showing lower mean amplitudes in the whole temperature range and the difference between both amplitude values is greater in the case of the heptacoordinated anion. This situation confirms again the influence of congestion effects in the IF₅ plane, which contribute in an important way to the I–F bond lengthening and weakening [82,122,124]. This also explains the weaker I–F bonds in the case of *trans*-F₅IO₂²⁻, when compared with *trans*-F₄IO₂⁻ [123,124].

4.3.5. F₂BrO₃⁻

This recently reported oxohalogen anion [125] is a very interesting example of a rather seldom molecular structure, i.e., a F₂EO₃ trigonal bipyramidal species with the three oxygen atoms occupying the equatorial positions and the two fluorine atoms located at the axial positions. Only two other molecules presenting this structure have so far been described; they are F₂XeO₃ [126] and the matrix isolated F₂O₃ [127].

The mean amplitudes of vibration of this anion, at some selected temperatures, and calculated on the basis of the known structural and spectroscopic data [125], are shown in Table 26 [128].

The results show some interesting and somewhat unexpected results. As can be seen from the data presented in Table 26, the amplitude values for the Br–O bonds present a relatively important temperature dependence, and an increment of about 35% is

Table 26

Mean amplitudes of vibration (in Å) of BrO₃F₂⁻ [128], at some selected temperatures

T (K)	u _{Br-O}	u _{Br-F}	u _{O...O}	u _{F...F}	u _{F...O}
0	0.0385	0.0481	0.059	0.063	0.051
298.16	0.0392	0.0534	0.065	0.072	0.057
400	0.0404	0.0579	0.069	0.078	0.062
600	0.0440	0.0673	0.080	0.091	0.072
800	0.0481	0.0760	0.089	0.103	0.082
1000	0.0522	0.0842	0.098	0.115	0.091

observed between 0 and 1000 K, pointing to a relative weakness of these bonds. In fact, they are even weaker than similar bonds in Br(V) species (cf. with values for F₃BrO, F₂BrO⁺ and F₄BrO⁻ in Tables 18, 20 and 22, respectively). The Br–F bonds are also relatively weak and present an important temperature dependence. For Br(VII) species their strength can be clearly correlated with the overall charge on these species, i.e., the positive BrF₆⁺ presents the strongest whereas the negatively charged F₂BrO₃⁻ anion shows the weakest Br–F bond; the neutral molecule FBrO₃ presents an intermediate strength (cf. Tables 8 and 17).

A comparison with the structurally related F₂XeO₃ molecule [129] shows that in this case, the Xe–O bonds are somewhat stronger than the Br–O bonds in F₂BrO₃⁻ although their mean amplitudes of vibration show a similar temperature dependence in both cases. On the other hand, the Xe–F mean amplitude values are the lowest so far calculated for a bond of this type [26,129] pointing to particularly strong Xe–F linkages (values, at 298.16 K, are: u_{Xe-O} = 0.0379 Å; u_{Xe-F} = 0.0434 Å [129]).

5. General trends and correlations

On the basis of the presented data it becomes possible to establish some general trends between the mean amplitudes of vibration and other molecular parameters and characteristics. In the case of hypervalent iodine compounds some of these trends have recently been emphasized [27] but they can now be extended and applied to all the reported systems, as follows:

- The mean amplitudes of vibration for the X–O bonds are highly characteristic. Observing, for example, the values obtained at 298.16 K they vary only between 0.0362 and 0.0388 Å in the case of I–O bonds, between 0.0349 and 0.0392 Å for Br–O bonds and between 0.0341 and 0.0386 Å for Cl–O bonds. These values are clearly located in the range that is considered as typical for these bonds [4] and, on the other hand, they are relatively strong, as suggested by their weak temperature dependence.
- On the contrary, the values for the X–F bonds cover, in all cases, a relatively wide range (0.0377–0.0602 Å for I–F, 0.0399–0.0591 Å for Br–F and 0.0412–0.0622 Å for Cl–F bonds) suggesting that these bonds depend strongly on the chemical peculiarities of the involved compound. In particular, it becomes evident that the oxidation state of the central atom, the ionic charge, the coordination number, and the presence of oxygen ligands or free electron pairs has an important effect on the properties of the X–F bonds.
- In the case of iodine, the extreme values are found for IF₆⁺ and IF₅²⁻, in agreement with the fact that in the first species iodine presents the oxidation state +7 and a positive charge whereas in the other one the iodine is in the oxidation state +3 and presents two negative charges. Besides, these two species present also the greatest differences in bond lengths found for I/F species (1.75 Å for IF₆⁺, 2.095 Å for IF₅²⁻ [122]). The anomalous high amplitude value found in the case of IF₅²⁻, which have also been observed in the case of the isoelectronic XeF₅⁻ anion [84], suggests relatively

weak bonds, undoubtedly related to an important congestion effect on the molecular plane, in which the fluorine atoms are practically in contact [81,84].

- The impact of a geometrical effect can also be seen by the comparison of *trans*-F₅IO₂²⁻ and *trans*-F₄IO₂⁻, in which the increment of the mean amplitude values in the first case, can be mainly attributed to the congestion effect in the equatorial IF₅ plane.
- For bromine the extreme Br–F values are found for BrF₄⁺ (equatorial bonds) and F₂BrO₂⁻, with BrF₆⁺ and BrF₂⁺ very close to the lowest limit. For chlorine the extreme amplitudes are found for ClF₂⁺ and F₂ClO₂⁻.
- It is evident that for species with identical ionic charge, those with a higher oxidation state of the central atom shall present lower mean amplitudes of vibration. This is well-illustrated by the comparison between XF₄⁻ and XF₂⁻ species (cf. Section 3.3.2).
- The peculiar bonding effects related to the two geometrically different I–F bonds in IOF₅ have been discussed in detail in Section 4.1.5. In the same manner, differences between equatorial and axial bonds in some of the investigated species are always in agreement with the predictions of the employed bonding model.
- Information concerning mean amplitude values of interhalogen bonds not involving fluorine atoms are very limited and at present it is impossible to establish any type of generalization for these bonds, although their general behavior seems to be comparable to that of the X–F bonds.
- The reviewed results also show that it is impossible to perform generalizations or to find trends in the case of the mean amplitudes of vibration of the non-bonded atomic pairs.
- In general, and as discussed on the basis of selected examples in the different sections of this review, all the species which are isoelectronic with the investigated molecules and ions behave in the expected manner, i.e., the mean amplitudes of vibration of anionic species are usually higher than those of their isoelectronic neutral counterparts, whereas the values for these are higher as those of the respective cationic species.
- The performed calculations also show that the analysis of the temperature dependences of amplitude values may be a useful criterion for the comparison and prediction of bond strengths. Besides, in the case of systems involving heavy atoms, this analysis also allows to detect the existence of the so called “low temperature anomalies”.

Finally, it is also important to remark that mean amplitudes of vibration obtained by calculation from spectroscopic data are very useful for the analysis and interpretation of electron diffraction experiments [1,130,131], and in this context the data tabulated and thoroughly discussed in this review may be of interest for future structural studies of gaseous molecules containing interhalogen or halogen–oxygen bonds.

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