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Mean Amplitudes of Vibration of the XF_4^+ Interhalogen Cations

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SUMMARY

Mean amplitudes of vibration for the cations ClF_4^+, BrF_4^+ and IF_4^+ have been calculated using the 'Method of the Characteristic Vibrations' and recently revised spectroscopic data. The results are briefly discussed and some comparisons with isoelectronic molecules and other related species are made.

INTRODUCTION

As part of our work dealing with the study of vibrational properties of species containing interhalogen bonds we have now done an estimation of the mean amplitudes of vibration of the XF_4^+ cations in order to obtain a wider insight into their structure and bond characteristics.

These ions possess C_{2v} symmetry and their structure can be derived from a sp^3d hybridisation 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.

The vibrational spectra of the three cations have been reported by Christe and Sawodny [1]. In the case of ClF_4^+, some of the deformations have been further reassigned by comparison with the spectroscopic data of the isoelectronic SF_4 molecule [2-4].

RESULTS and DISCUSSION

The fundamental vibrations for the three cations, together with the proposed assignments [5] , are shown in Table 1 and the corresponding structural parameters in Table 2.

To perform the calculation of the mean amplitudes of vibration we have used, as in other similar cases, the method of the characteristic vibrations of Müller [6-8] . The obtained values, at different temperatures, are reported in Table 3.

TABLE 1

Fundamental Vibrations of the XF_4^+ Ions (in cm^{-1})

Species		ClF_4^+	BrF_4^+	IF_4^+	Assignment
A_1	ν_1	800	723	704	ν_s XF_2 eq
	ν_2	571	606	609	ν_s XF_2 ax
	ν_3	515	419	385	δsciss.XF_2 eq
	ν_4	250	216	151	δsciss.XF_2 ax
A_2	ν_5	(450)	-	-	XF_2 twist
B_1	ν_6	795	704	655	ν_{as} XF_2 ax
	ν_7	475	385	341	XF_2 eq wagg.
B_2	ν_8	829	736	720	ν_{as} XF_2 eq
	ν_9	385	369	316	δsciss.ax out plane

TABLE 2

Structural Parameters of the Investigated Cations

Cation	$r_{X-F(ax)}$	$r_{X-F(eq)}$	$\widehat{FXF}$(eq)	$\widehat{FXF}$(ax)	Refer.
ClF_4^+	1.66 Å	1.57 Å	97°	180°	[1]
BrF_4^+	1.85 Å	1.77 Å	96°	173°	[9]
IF_4^+	1.83 Å	1.79 Å	107°	148°	[10]

TABLE 3

Calculated Mean Amplitudes of Vibration (in Å)

Cation	Distance	0 K	298 K	500 K
ClF_4^+	Cl-F(ax)	0.0440	0.0458	0.0507
	Cl-F(eq)	0.0409	0.0417	0.0450
	$F_{ax}F_{ax}$	0.056	0.059	0.068
	$F_{eq}F_{eq}$	0.054	0.058	0.066
	$F_{ax}F_{eq}$	0.059	0.065	0.077
BrF_4^+	Br-F(ax)	0.0408	0.0426	0.0476
	Br-F(eq)	0.0388	0.0399	0.0439
	$F_{ax}F_{ax}$	0.054	0.058	0.065
	$F_{eq}F_{eq}$	0.058	0.065	0.076
	$F_{ax}F_{eq}$	0.062	0.071	0.084
IF_4^+	I-F(ax)	0.0402	0.0421	0.0473
	I-F(eq)	0.0378	0.0391	0.0431
	$F_{ax}F_{ax}$	0.052	0.057	0.065
	$F_{eq}F_{eq}$	0.058	0.065	0.076
	$F_{ax}F_{eq}$	0.065	0.077	0.092

It is interesting to make some comparisons among these results and also with the corresponding values of some related species.

The mean amplitudes of the axial X-F bonds are always larger than the corresponding amplitudes of the equatorial bonds. This is in agreement with the structural data reported in Table 2, which show that the axial bonds are slightly longer than the equatorial. The amplitude values for the bonded atoms decrease from the ClF_4^+ to BrF_4^+ and then remains practically constant to IF_4^+. A similar trend is observed in the corresponding series of XF_4^- anions [11] as well as in the isoelectronic SF_4, SeF_4 and TeF_4 molecules [12] .

Furthermore, comparison of isoelectronic species shows a slight decrease in the mean amplitudes of the axial bonds, going from the molecule to the ion, whereas the equatorial values remain practically unchanged. In an isoelectronic series of this type a diminution of the amplitude values with the increase of positive charge is expected [13] in accordance with a strengthening of the bonds in that direction. The present results show, that the stronger (equatorial) bonds are less affected by the charge increase than the corresponding axial bonds, pointing to slight differences in the bond properties of the two types of X-F bonds present in these species.

On the other hand, the mean amplitude values for the equatorial bonds lie close to those of the corresponding trivalent XF_2^+ [14] and heptavalent XF_6^+ [15,16] cations. In general, both X-F amplitude values of the XF_4^+ ions lie also lower than those computed for species such as XOF_4^+ [17] or XF_5 [18] in which the interhalogen bonds possess a partial ionic character.

In conclusion, the amplitude values found in the present study point to relatively strong interhalogen bonding, specially in the case of the equatorial bonds. It appears that the axial bonds are more polar than the equatorial ones. This polar character diminishes with the increase of atomic number of the central halogen atom and both types of X-F bonds become more and more similar.

Finally, it is also worth commenting that the mean amplitudes for the non bonded pairs are very similar for the three cations and also in a given species the values for the $F_{eq}F_{eq}$ and $F_{ax}F_{ax}$ pairs are similar whereas those corresponding to the $F_{ax}F_{eq}$ pairs are always higher.

On the other hand, it must be pointed out that mean amplitudes of vibration are generally not very sensitive towards changes in assignment (see for example [2-4] for SF_4) although they may be useful in the detection of gross errors in the assignments or to obtain a wider insight into structural peculiarities [19,20].

All the calculations were performed using an IBM/360 computer (CESPI-Universidad Nacional de La Plata).

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