Journal of Fluorine Chemistry 130 (2009) 534–536

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Mean amplitudes of vibration of the ClF_6^-, BrF_6^- and IF_6^- anions

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ARTICLE INFO

Article history:
Received 26 January 2009
Received in revised form 25 February 2009
Accepted 5 March 2009
Available online 5 April 2009

Keywords:
$ClF_6(-)$
$BrF_6(-)$
$IF_6(-)$
Mean amplitudes of vibration
Bond properties

ABSTRACT

Mean amplitudes of vibration for the title hexafluoroanions were calculated on the basis of its vibrational-spectroscopic and structural data in the temperature range between 0 and 1000 K. The results are briefly discussed in comparison with those of other related species.

1. Introduction

The three halogen hexafluoroanions, XF_6^-, are interesting species concerning their structural characteristics and peculiarities as they belong to the hypervalent XF_6E class of compounds (formally sp^3d^3 hybridization of the central atom) that contain six fluorine ligands and one lone electronic pair E. Although different types of studies have been performed with these anions during the last 30 years [1–6], only recently their vibrational-spectroscopic behavior could be definitively clarified in a unified view [7].

On the basis of the valence-shell electron-pair repulsion (VSEPR) model [8–11] one may expect a distorted octahedral structure for these anions, in which E becomes sterically active. Notwithstanding, in the case of ClF_6^- and BrF_6^- both, spectroscopic [3,4,7] and structural [5] investigations, clearly demonstrate a practically perfect octahedral symmetry. On the contrary, the geometry of IF_6^- is a strongly distorted octahedron with approximately C_{3v} symmetry [6] a fact not totally unexpected as this anion is isoelectronic with XeF_6. In IF_6^- three fluorine atoms have shorter I–F bonds (between 1.82 and 1.89 Å) that form angles minor than 90° with each other, whereas the other three are longer (between 1.95 and 2.11 Å) with angles greater than 90° [6].

The commented structural differences between the three anions can be attributed to the different sizes of the central halogen atoms. In the smaller chlorine and bromine atoms, the six ligands are close-packed leaving no room in the valence shell for a lone pair [9,10]. So there is, in fact, no lone pair in these species, and the two non-bonding electrons are forced to remain associated with the core forming a spherical shell around the inner core [10]. As shown by recent theoretical calculations the lone pair is found essentially in the symmetric A_{1g} molecular orbital, i.e. presenting an important s character [7]. In the case of IF_6^-, with a larger central atom, the fluorine ligands are not quite close-packed, allowing room for some of the non-bonding electron density to move into the valence shell to form what has been called a partial or weak lone pair, resulting in the observed C_{3v} distortion of the octahedral structure [3,7,10].

As part of our studies devoted to the calculation of mean amplitudes of vibration and other bond properties of simple species containing halogen–halogen and/or halogen–oxygen bonds (for a recent review cf. [12]) we have now calculated the mean amplitudes of vibration of these three anions.

2. Calculations

The calculations were performed with the method of the "characteristic vibrations" of Müller et al. [13] (cf. also [14,15]), which has provided excellent results for a wide range of molecular systems of different symmetries and bonding characteristics [12].

For the octahedral anions ClF_6^- and BrF_6^- the calculations were performed in the way described earlier [16]. The necessary vibrational-spectroscopic data were taken from Ref. [7] and all F–X–F angles were considered equal to 90°. On the other hand, for the distorted IF_6^- anion the employed vibrational data, taken by a combination of experimental [2] and theoretical [7] results, are presented in Table 1. Regarding the geometric parameters, for the F–I–F angles involving the shorter I–F bonds a mean value of 82°

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doi:10.1016/j.jfluchem.2009.03.009

Table 1
Vibrational-spectroscopic data for the IF_6^- anion.

Mode	Description[a]	Frequency (cm^{-1})
ν_1 (A_1)	ν_s(I–F)	620
ν_2 (A_1)	ν_s(I–F*)	451
ν_3 (A_1)	$\delta(IF_3)$	347
ν_4 (A_1)	$\delta(IF_3^*)$	199
ν_5 (A_2)	$\rho_t(IF_6)$	275
ν_6 (E)	ν_{as}(I–F)	600
ν_7 (E)	ν_{as}(I–F*)	390
ν_8 (E)	$\delta_{sciss}(IF_3)$	347
ν_9 (E)	$\delta_{sciss}(IF_3^*)$	260
ν_{10} (E)	$\rho_r(IF_6)$	58

[a] IF refers to the shorter I–F bonds, IF* to the longer bonds.

Table 2
Mean amplitudes of vibration (in Å) for the ClF_6^- anion in the temperature range between 0 and 1000 K.

T (K)	u_{Cl-F}	$u_{F\cdots F}$ (short)	$u_{F\cdots F}$ (long)
0	0.0514	0.078	0.066
100	0.0515	0.080	0.067
200	0.0534	0.090	0.070
298.16	0.0572	0.102	0.077
300	0.0573	0.103	0.077
400	0.0620	0.115	0.085
500	0.0669	0.127	0.092
600	0.0718	0.138	0.10
700	0.0765	0.148	0.106
800	0.0810	0.158	0.113
900	0.0854	0.167	0.120
1000	0.0896	0.176	0.126

was employed, whereas for the angles between the longer bonds an angle of 111° was used (cf. [6]). This also means that in the case of IF_6^- two groups of mean amplitude values were obtained, one set for the shorter and another one for the longer I–F bonds.

The calculations were performed in the usual temperature range, between 0 and 1000 K, despite the fact that these species are not stable at high temperatures. Notwithstanding, the calculations in such an extended range allow often to detect interesting and unexpected vibrational peculiarities.

3. Results and discussion

The mean amplitudes of vibration for ClF_6^- and BrF_6^-, in the temperature range between 0 and 1000 K are shown in Tables 2 and 3, respectively. As it can be immediately seen, the mean amplitude values for the Br–F bonds are always lower than those of the Cl–F bonds, pointing to somewhat stronger X–F bonds in the BrF_6^- anion. Values calculated for IF_6^- are shown in Table 4 and, as

Table 3
Mean amplitudes of vibration (in Å) for the BrF_6^- anion in the temperature range between 0 and 1000 K.

T (K)	u_{Br-F}	$u_{F\cdots F}$ (short)	$u_{F\cdots F}$ (long)
0	0.0458	0.082	0.061
100	0.0459	0.085	0.061
200	0.0470	0.099	0.063
298.16	0.0498	0.115	0.067
300	0.0498	0.115	0.067
400	0.0536	0.130	0.073
500	0.0577	0.144	0.078
600	0.0617	0.156	0.084
700	0.0657	0.168	0.090
800	0.0695	0.179	0.095
900	0.0732	0.190	0.100
1000	0.0768	0.200	0.105

Table 4
Mean amplitudes of vibration (in Å) for the IF_6^- anion in the temperature range between 0 and 1000 K[a].

T (K)	u_{I-F} (short)	u_{I-F} (long)	$u_{F\cdots F}$ (short)	$u_{F\cdots F}$ (long)
0	0.0409	0.0495	0.065	0.073
100	0.0409	0.0496	0.066	0.074
200	0.0414	0.0520	0.070	0.082
298.16	0.0431	0.0567	0.077	0.092
300	0.0431	0.0568	0.077	0.092
400	0.0457	0.0622	0.084	0.103
500	0.0487	0.0676	0.092	0.113
600	0.0518	0.0729	0.099	0.123
700	0.0548	0.0780	0.106	0.132
800	0.0578	0.0828	0.113	0.140
900	0.0608	0.0874	0.119	0.149
1000	0.0637	0.0919	0.125	0.156

[a] (short) refers to the IF_3 fragment with shorter I–F bonds and smaller angles and (long) refers to the IF_3 fragment with longer I–F bonds and greater angles.

Table 5
Mean amplitudes of vibration (in Å), at 298.16 K, for different interhalogenated species related to the investigated XF_6^- anions.

Species	u_{Cl-F}	u_{Br-F}	u_{I-F}	Reference
ClF_6^-	0.0572			This work
BrF_6^-		0.0498		This work
IF_6^-			0.0431 (sh)	This work
			0.0567 (lg)	This work
ClF_4^+	0.0458 (ax)			[17]
	0.0417 (eq)			
BrF_4^+		0.0426 (ax)		[17]
		0.0399 (eq)		
IF_4^+			0.0421 (ax)	[17]
			0.0391 (eq)	
ClF_5	0.0462 (ax)			[18]
	0.0507 (eq)			
BrF_5		0.0422 (ax)		[18]
		0.0452 (eq)		
IF_5			0.0394 (ax)	[18]
			0.0430 (eq)	
$FClO_2$	0.0487			[19]
$FBrO_2$		0.0508		[20]
$F_2ClO_2^-$	0.0622			[21]
$F_2BrO_2^-$		0.0591		[22]
$F_2IO_2^-$			0.0534	[23]
F_4ClO^-	0.0555			[24]
F_4BrO^-		0.0521		[24]
F_4IO^-			0.0501	[24]

(ax) refers to axial X–F bonds and (eq) to equatorial X–F bonds.
(sh) refers to the shorter and (lg) to the longer I–F bonds in IF_6^-.

it can be seen, the shorter I–F bonds present mean amplitudes which are even lower than those of the bromine species.

Interestingly, recently performed high-level theoretical calculations of thermodynamic data of iodine fluorides and related species also show that the average bond dissociation energies goes in the order $IF_6^- > BrF_6^- > ClF_6^-$ [7].

In order to have a wider insight into the peculiarities and characteristics of all these X–F bonds it seems interesting to compare the obtained results with those of some other interhalogenated species in which the central atom presents also the same formal charge (+5) as in the three investigated anions. These comparisons are performed in Table 5.

The amplitude values calculated here for the three XF_6^- anions are clearly found in the ranges which can be considered as typical for the different X–F bonds [12]. As expected, both the XF_4^+ and the XF_5 species present lower mean amplitudes of vibration, and

therefore stronger bonds, than the respective XF_6^- anions. In the case of the oxygenated species, $FClO_2$ has a stronger Cl–F bond than ClF_6^- whereas the Br–F bond of $FBrO_2$ is somewhat weaker than those of the BrF_6^- anion. A comparison with the $F_2XO_2^-$ species shows the presence of X–F bonds which are weaker then those of the XF_6^- anions, a fact which is not totally unexpected as these oxoanions present very strong X–O bonds which contribute to the enhancement of the ionic character of the axial X–F bonds that may be considered as semi-ionic 3c–4e bonds [12]. Finally, a comparison with the square–pyramidal F_4XO^- anions shows that ClF_6^- has weaker Cl–F bonds than F_4ClO^- whereas the Br–F and the shorter I–F bonds of the hexafluoroanions are stronger than those of the respective oxoanions.

Regarding the non-bonded F···F pairs of ClF_6^- and BrF_6^-, that at shorter distances show somewhat higher amplitude values in the second case, whereas the longer bonds present higher values for the chlorine species. In IF_6^- the mean amplitudes calculated for the non-bonded F···F interactions in the case of the shorter I–F bonds are always lower than those related to the longer I–F bonds.

To conclude, the now performed calculations extends our knowledge on mean amplitudes of vibration for species with interhalogen bonds. The behavior of the investigated XF_6^- anions satisfactorily fulfills all of the general trends and correlations discussed recently [12] and shows the presence of species containing X–F bonds of intermediate strength.

Acknowledgements

The support of the "Consejo Nacional de Investigaciones Científicas y Técnicas de la República Argentina"—CONICET is highly acknowledged. The author is a member of the Research Career of this organism.

References

[1] K.O. Christe, J.P. Guertin, W. Sawodny, Inorg. Chem. 7 (1968) 626–628.
[2] K.O. Christe, Inorg. Chem. 11 (1972) 1215–1219.
[3] K.O. Christe, W.W. Wilson, Inorg. Chem. 28 (1989) 3277–3278.
[4] K.O. Christe, W.W. Wilson, R.V. Chirakal, J.C.P. Sanders, G.J. Schrobilgen, Inorg. Chem. 29 (1990) 3506–3511.
[5] A.R. Mahjoub, A. Hoser, J. Fuchs, K. Seppelt, Angew. Chem. Int. Ed. Engl. 28 (1989) 1526–1528.
[6] A.R. Mahjoub, K. Seppelt, Angew. Chem. Int. Ed. Engl. 30 (1991) 323–324.
[7] D.A. Dixon, D.J. Grant, K.O. Christe, K.A. Peterson, Inorg. Chem. 47 (2008) 5485–5494.
[8] R.J. Gillespie, I. Hargittai, The VSEPR Model of Molecular Geometry, Allyn and Bacon, Boston, 1991.
[9] R.J. Gillespie, E.A. Robinson, Chem. Soc. Rev. 34 (2005) 396–407.
[10] R.J. Gillespie, Coord. Chem. Rev. 252 (2008) 1315–1327.
[11] D.M.P. Mingos, Essential Trends in Inorganic Chemistry, Oxford University Press, Oxford, 1998.
[12] E.J. Baran, J. Fluor. Chem. (2008) 1060–1072.
[13] A. Müller, C.J. Peacock, H. Schulze, U. Heidborn, J. Mol. Struct. 3 (1969) 252–255.
[14] A. Müller, E.J. Baran, K.H. Schmidt, in: S.J. Cyvin (Ed.), Molecular Structures and Vibrations, Elsevier, Amsterdam, 1972, pp. 376–391.
[15] E.J. Baran, An. Asoc. Quím. Argent. 61 (1973) 141–151.
[16] E.J. Baran, Monatsh. Chem. 105 (1974) 362–365.
[17] E.J. Baran, J. Fluor. Chem. 17 (1981) 543–548.
[18] S.J. Cyvin, J. Brunvoll, A. Robiette, J. Mol. Struct. 3 (1969) 259–261.
[19] E.J. Baran, Z. Chem. 13 (1973) 391–392.
[20] E.J. Baran, Spectr. Lett. 9 (1976) 323–327.
[21] E.J. Baran, Monatsh. Chem. 107 (1976) 1303–1305.
[22] E.J. Baran, Z. Naturforsch. 56a (2001) 601–602.
[23] E.J. Baran, Indian J. Pure Appl. Phys. 15 (1977) 450–451.
[24] E.J. Baran, Monatsh. Chem. 110 (1979) 715–719.