

# IR-spectroscopy of $\text{XF}_3$ and $\text{XF}_5$ interhalides ( $\text{X} = \text{Cl}$ and $\text{Br}$ )

Sh.Sh. Nabiev

Russian Scientific Center "Kurchatov Institute," Moscow

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IR absorption spectra of  $\text{XF}_3$  and  $\text{XF}_5$  ( $\text{X} = \text{Cl}$  and  $\text{Br}$ ) molecules in gas phase and cryogenic solutions of Kr ( $T = 130$  K) and Xe ( $T = 180$  K) within wide range of frequencies ( $200\text{--}2500\text{ cm}^{-1}$ ) including the range of the 3rd order transitions were studied. Integral value of the absorption coefficient of the  $\nu_7(E)$  band of  $\text{XF}_5$  has been determined, as well as relative intensities of all bands observed in the  $\text{XF}_5$  infrared spectrum and anharmonicity constants for some  $\text{XF}_3$  and  $\text{XF}_5$  vibrations. It is shown that contrary to  $\text{BrF}_3$ , a splitting of asymmetrical vibration band into  $(\text{Cl-F})_{\text{ax}}$  bonds of  $\text{ClF}_3$  is due to Coriolis interaction between energetically close levels  $\nu_1(A_1)$  and  $\nu_4(B_1)$  when the molecule rotates about the axis of maximum moment of inertia. Based on analysis of spectroscopic data, results of *ab initio* calculations, as well as estimates of the polarization  $d$ -functions importance for central atom and effects of electron correlation, the conclusion was drawn that the model for calculating the infrared intensities for  $\text{XF}_3$  ( $\text{X} = \text{Cl}$  and  $\text{Br}$ ) molecules should take into account both the difference in characters of  $(\text{X-F})_{\text{ax}}$  and  $(\text{X-F})_{\text{eq}}$  bonds and contributions from nonrigid intramolecular groupings according to tourniquet mechanism.

## Introduction

In recent years, interhalides of  $\text{XF}_3$  and  $\text{XF}_5$  type ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ ) have gained an extensive use in various branches of science and technology. The halogen fluorides, as fluoridating agents, are widely used in water free ("dry") processes of nuclear materials processing.<sup>1,2</sup> Besides, these compounds are used actively in chemical, electronic, and metallurgy industry, for example, in synthesis of power-consuming complex fluorine-containing compounds,<sup>3-5</sup> gas-phase etching of semiconductors, smelting and cutting of refractory metals,<sup>6,7</sup> and are also of certain interest for laser technology and production of chemical sources of electric current.<sup>8</sup> Finally, interhalides are the components of jet fuels and propellants. The hypergolic properties of these compounds can be used in solid propellants.<sup>9</sup>

At the same time Cl and Br fluorides can be very toxic and chemically active components of the emergency emission plumes from the aforementioned industries.<sup>10</sup> These compounds actively interact with water vapor and other gaseous components of the atmosphere. This results in formation of molecules of hydrogen halides, oxyfluorides, and Cl and Br oxides, which, in their turn, can be easily transformed into stable molecular complexes of donor-acceptor type<sup>11</sup>  $(\text{HHal})_x \dots (\text{H}_2\text{O})_y$ , where  $\text{Hal} = \text{F}$ ,  $\text{Cl}$ , and  $\text{Br}$ ;  $x + y \geq 2$ . In order to study the mechanisms of reactions involving  $\text{XF}_3$  and  $\text{XF}_5$  ( $\text{X} = \text{Cl}$  and  $\text{Br}$ ) and their secondary compounds in the atmosphere and to analyze the applicability limits of the methods of remote laser diagnostics, more comprehensive information on the interhalides vibrational spectra is needed.

The Cl and Br trifluorides and pentafluorides were first synthesized quite many years ago.<sup>6,7,12</sup> Nevertheless, the information on vibrational spectra of  $\text{XF}_3$  and  $\text{XF}_5$  ( $\text{X} = \text{Cl}$  and  $\text{Br}$ ) compounds is not abundant. Data on spectroscopic parameters like anharmonicity constants, isotopic shifts of vibrational frequencies, as well as absolute and relative strengths of fundamental, combination, and overtone transitions, including the transition range of high ( $\nu \geq 3$ ) order, are practically unavailable.

In this work, we have studied the IR absorption spectra of  $\text{XF}_3$  and  $\text{XF}_5$  molecules ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ ) in gas phase ( $T = 300$  K) and in solutions of liquefied gases Kr ( $T = 130$  K) and Xe ( $T = 180$  K) in a wide frequency range ( $200\text{--}2500\text{ cm}^{-1}$ ). The advantages of the cryogenic method over the gas spectroscopy are well known.<sup>13</sup> We pay particular attention to mechanisms of the compounds chemical transformation under conditions of their interaction with atmospheric moisture, as well as to determination of integral absorption coefficients for vibrational bands falling into the range used for operation of lidars (including multifrequency ones) based on mid-infrared molecular lasers.

## 1. Experiment

The main units of the experimental setup, described in detail in Refs. 14 and 15, were a set of gas cells and cryostats; IR-spectrophotometers; bottles with  $\text{XF}_3$  and  $\text{XF}_5$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ ), fluorine, and noble gases; a system for intake of the gases under study and gas-solvents, and sensors for the temperature and pressure control.

The infrared spectra of the  $\text{XF}_3$  and  $\text{XF}_5$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ ) specimens were recorded with the help of dual-channel diffraction spectrophotometers "Perkin Elmer-325" and "Specord-75 IR" with the entrance slits spectral width of  $0.8$  to  $1.5\text{ cm}^{-1}$ . Calibration of the spectrophotometers' wave number scale was performed using  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ , and  $\text{H}_2\text{O}$  spectra and data from Ref. 16. Within the frequency range lower than  $1000\text{ cm}^{-1}$ , the spectrum was corrected for the negative light fluxes.<sup>17</sup> Relative error in the integral absorption coefficients determined for most intensive bands in the IR-spectra of  $\text{XF}_3$  and  $\text{XF}_5$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ ) in cryogenic solutions did not exceed 15%. The values of the vibration bands' half-widths were corrected for final width of the slit according to Ref. 18. The values of the integral absorption coefficients for free molecules were recalculated by the following formula<sup>13</sup>

$$A_{\text{gas}} = A_{\text{sol}} [9n/(n^2 + 2)^2] = K(n) A_{\text{sol}}, \quad (1)$$

where  $n$  is the refractive index of a cryogenic solution. For liquid Ar ( $T \cong 90$  K)  $n = 1.23$ , for Kr ( $T \cong 130$  K)  $n = 1.29$ , and for Xe ( $T \cong 180$  K)  $n = 1.39$ . The correcting coefficient

$K(n)$  takes into account a set of factors mainly related to change of the strength of light field incident onto a cryogenic solution as compared that in vacuum.

Pressure in the gas intake system was monitored by the pressure sensors DP-5, "Sapfir-22DA," and manometers; the temperature of the cryostat working volume was measured using a specially designed thermometer. The measurements of cryogenic solution temperature were conducted by Chromel-Alumel and copper-constantan thermocouples introduced into the cryostats' working volumes. We used multipass gas cells based on White optical arrangement allowing the length of the optical path to be varied from 12 to 100 cm, as well as cryostat cells with the length of optical path of 3.5 to 10 cm.

In preparing the  $\text{XF}_3$  and  $\text{XF}_5$  ( $X = \text{Cl}, \text{Br}$ ) solutions in liquid Kr and Xe, we used the technique of dissolving crystal phase samples of these compounds in a liquid noble gas.<sup>19</sup> To do this, some amount of  $\text{XF}_3$  and  $\text{XF}_5$  was frozen on thoroughly passivated inner walls of the cryostat's working chamber, on which the noble gas was then condensed. The  $\text{XF}_3$  and  $\text{XF}_5$  samples were thoroughly purified. According to the data of quantitative analysis conducted by the method described in Ref. 20, the concentration of impurities, like HF,  $\text{CF}_4$ , and so on, in the samples of interhalides was lower than 0.1%.

The accuracy of determination of the  $\text{XF}_3$  and  $\text{XF}_5$  concentration in the cryogenic solutions was 5–10%, and their temperature was maintained constant accurate to  $\pm 2$  K.

## 2. The character of chemical bonds, structure, and peculiarities of $\text{XF}_3$ and $\text{XF}_5$ ( $X = \text{Cl}, \text{Br}$ ) hydrolysis

In accordance with the reactivity, the halide-fluorides  $\text{XF}_3$  and  $\text{XF}_5$  ( $X = \text{Cl}, \text{Br}$ ) form the row<sup>21</sup>

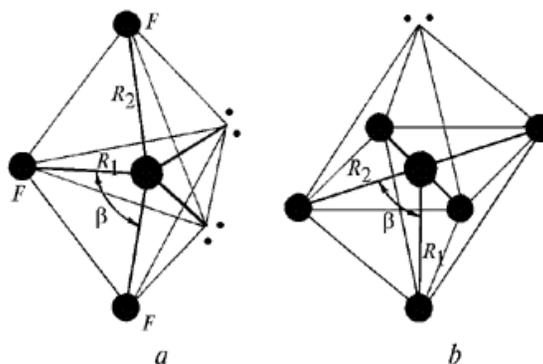


and in some cases the chemical activity of these compounds significantly exceeds that of molecular fluorine.<sup>7,8</sup> Some of their most important physical-chemical constants are given in Table 1.

**Table 1. Chemico-physical properties of  $\text{XF}_3$  and  $\text{XF}_5$  molecules ( $X = \text{Cl}, \text{Br}$ )**

Property	Value			
	$\text{ClF}_3$	$\text{BrF}_3$	$\text{ClF}_5$	$\text{BrF}_5$
Energy of X-F bond, kcal mol <sup>-1</sup>	38.2	48.1	36.8	44.7
Valence force constants				
X-F <sub>ax</sub> , mdin/Δ:	2.704	4.084	3.331	4.248
X-F <sub>eq</sub> , mdin/Δ:	4.193	3.009	2.991	3.423
Dipole moment, D	0.557	1.190	–	1.510
T <sub>fus</sub> , K	196.8	281.9	181.0	212.7
T <sub>boil</sub> , K	284.9	398.9	260.3	314.5
ΔH <sub>fus</sub> , kcal mol <sup>-1</sup>	1.82	2.88	0.383	1.76
ΔH <sub>vap</sub> , kcal mol <sup>-1</sup>	6.58	10.24	5.74	7.31
ΔS <sub>vap</sub> , e.u.	23.1	25.7	21.8	23.3
Δ <sub>298</sub> <sup>0</sup> (g), kcal mol <sup>-1</sup>	-39.35	-61.1	-57.7	-106.2
Vapor pressure (300 K), Torr	1530.6	13.5	2855.0	390.3

Among the diversity of molecules of  $\text{XY}_3$  type,  $\text{ClF}_3$  and  $\text{BrF}_3$  hold a special position due to their unusually plane T-shape structure. So, for  $\text{ClF}_3$  this structure is stipulated by the transition of one of 3p-electrons in Cl atom to 3d-orbital ( $\text{Cl}^*$ ):  $\text{Cl}^0 \rightarrow 3s^2 3p_x^2 3p_y^2 3p_z^1$ ;  $\text{Cl}^* \rightarrow 3s^2 3p_x^2 3p_y^1 3p_z^1 3d_{xy}^1$ . This results in a trigonal pyramid  $sp^3 d$  ( $\text{XY}_3 E_2$ -configuration) consisting of three atoms of fluorine and two disconnected electron pairs with Cl atom at the center (Fig. 1a).



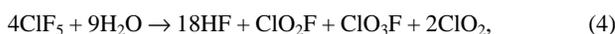
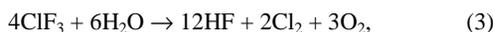
**Fig. 1.** Geometry of  $\text{XF}_3$  (a) and  $\text{XF}_5$  (b) molecules.  $\text{ClF}_3$  –  $\beta = 87.29^\circ$ ,  $R_1 = 1.698 \text{ \AA}$ ,  $R_2 = 1.598 \text{ \AA}$ ;  $\text{BrF}_3$  –  $\beta = 86.13^\circ$ ,  $R_1 = 1.810 \text{ \AA}$ ,  $R_2 = 1.721 \text{ \AA}$ ;  $\text{ClF}_5$  –  $\beta = 86.0^\circ$ ;  $R_1 = 1.571 \text{ \AA}$ ,  $R_2 = 1.669 \text{ \AA}$ ;  $\text{BrF}_5$  –  $\beta = 84.13^\circ$ ,  $R_1 = 1.774 \text{ \AA}$ ,  $R_2 = 1.721 \text{ \AA}$ .

In  $\text{ClF}_3$  and  $\text{BrF}_3$  molecules two fluorine atoms are positioned axially, two disconnected pairs ( $E_1$  and  $E_2$ ) and the third fluorine atom – equatorially. In this case  $\angle F_{ax}-Cl-F_{eq} = 87.29^\circ$ ,  $R(\text{Cl}-F_{ax}) = 1.698 \text{ \AA}$ ,  $R(\text{Cl}-F_{eq}) = 1.598 \text{ \AA}$  (gas),<sup>22</sup>  $\angle F_{ax}-Cl-F_{eq} = 86.59^\circ$ ,  $R(\text{Cl}-F_{ax}) = 1.716 \text{ \AA}$ ,  $R(\text{Cl}-F_{eq}) = 1.621 \text{ \AA}$  (solid).<sup>23</sup> For Br trifluorides  $\angle F_{ax}-Br-F_{eq} = 86.13^\circ$ ,  $R(\text{Br}-F_{ax}) = 1.810 \text{ \AA}$ ,  $R(\text{Br}-F_{eq}) = 1.721 \text{ \AA}$  (gas)<sup>24</sup>;  $\angle F_{ax}-Br-F_{eq} = 86.27^\circ$ ,  $R(\text{Br}-F_{ax}) = 1.85 \text{ \AA}$ ,  $R(\text{Br}-F_{eq}) = 1.72 \text{ \AA}$  (solid).<sup>25</sup> The above data indicate that the T-shape structure of  $\text{XF}_3$  molecules both in the gas<sup>22,24</sup> and solid<sup>23,25</sup> phase is slightly distorted ( $\angle F_{ax}-X-F_{ax} \cong 175^\circ$ ), and the valence bonds' lengths and angles well correspond to ideas of significant repulsion between disconnected electron pairs.<sup>26</sup>

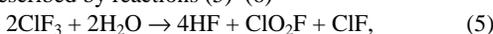
The  $\text{ClF}_5$  and  $\text{BrF}_5$  molecules have a structure of tetragonal pyramid, which, for example, for  $\text{ClF}_5$  is due to the transition of two electrons from the p-orbital to d-orbital. On the transition of one electron, the conditions appear which are equivalent to those needed to produce  $\text{ClF}_3$ :  $\text{Cl}^0 \rightarrow 3s^2 3p_x^2 3p_y^2 3p_z^1$ ;  $\text{Cl}^* \rightarrow 3s^2 3p_x^2 3p_y^1 3p_z^1 3d$ . On transition of the second electron, the conditions appear that favor the formation of five bonds with F-atoms:  $\text{Cl}^{*2} \rightarrow 3s^2 3p_x^1 3p_y^1 3p_z^1 3d_{xy}^1 3d_{yz}^1$ . This results in a tetragonal pyramid  $sp^3 d^2$  ( $\text{XY}_5 E$ -configuration), four F atoms of which are located in the corners of the square forming the foot plane with the fifth F-atom and a pair of unbound electrons ( $E$ ) being on the axes (Fig. 1b). Structure parameters of the  $\text{XF}_5$  ( $X = \text{Cl}, \text{Br}$ ) molecules deduced from microwave spectra<sup>27,28</sup> are as follows:  $R(\text{Cl}-F_{ax}) = 1.571 \text{ \AA}$ ,  $R(\text{Cl}-F_{eq}) = 1.669 \text{ \AA}$ ,  $\angle F_{ax}-Cl-F_{eq} = 86.0^\circ$ ;  $R(\text{Br}-F_{ax}) = 1.774 \text{ \AA}$ ,  $R(\text{Br}-F_{eq}) = 1.721 \text{ \AA}$ ,  $\angle F_{ax}-Br-F_{eq} = 84.13^\circ$ . As is seen from the above structure data, the configuration of distorted octahedron is realized for  $\text{XF}_5$  ( $X = \text{Cl}, \text{Br}$ ) molecules.<sup>29</sup> This is caused by the fact that the pair of unbound electrons positioned along the forth order axis interacts in different

manner with the binding electron pairs. This results in a slight change of angles between the binding pairs and the length of the neighbor bonds stretches because the repulsion of *cis*-electron pairs is stronger than that for a pair in the *trans*-configuration. As a result, the axial bond in  $\text{XF}_5$  becomes stronger than the equatorial ones. The influence on Cl and Br atoms therewith becomes relatively weaker, because they are less electronegative as compared with F.<sup>12,30</sup> The nonempirical calculations by the Hartree–Fock–Ruthan method<sup>12,31</sup> demonstrate that the bond in Br fluorides is more polar than in similar compounds of Cl. So, the complete population of Br and F atoms are 0.59 and 1.41, respectively, and the center-of-mass is shifted by 0.61 a.u. from the Br–F bond center to F atom.

The Cl and Br trifluorides and pentafluorides react practically with all elements of the periodic table except the elements of the VIII B group and some platinum metals.<sup>7,8,32</sup> These compounds demonstrate particularly active interaction with the atmospheric moisture. The course of hydrolysis reactions is a bit different for  $\text{XF}_3$  and  $\text{XF}_5$  ( $\text{X} = \text{Cl}, \text{Br}$ ) and depends on the reagents composition.<sup>33</sup> For example, hydrolysis of Cl trifluoride and pentafluoride at an excess of moisture content ( $\text{ClF}_3:\text{H}_2\text{O}, \text{ClF}_5:\text{H}_2\text{O} \leq 2:3$ ) follows the schemes (3–4)



whereas at the excess of  $\text{ClF}_3$  and  $\text{ClF}_5$  the hydrolysis process is described by reactions (5)–(6)

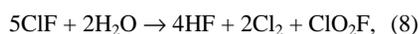


In the course of (4)–(6) reactions the chlorylfluoride is produced, which, in its turn, is slowly hydrolyzed thus producing HF,  $\text{ClO}_2$ , and  $\text{O}_2$ <sup>33,34</sup>



It should be noted that in the process of reactions (4) and (7) a fraction of  $\text{ClO}_2$  molecules can decompose into Cl and  $\text{O}_2$ .  $\text{O}_2$  therewith presumably oxidizes  $\text{ClO}_2\text{F}$  to inert (as compared with other Cl oxyfluorides)  $\text{ClO}_3\text{F}$ .

Hydrolysis of the chemically active Cl monofluoride (reaction (5)) at excess of  $\text{H}_2\text{O}$  proceeds similarly to (3), at the excess of ClF it yields HF,  $\text{Cl}_2$ , and  $\text{ClO}_2\text{F}$ <sup>7,12</sup>



and chlorylfluoride is then hydrolyzed following scheme (7).

Besides the chemically stable compounds, it is possible the formation, as intermediates in the hydrolysis, of unstable ClOF (enthalpy of formation  $\Delta H_{298}^0 = -46.1 \text{ kJ}\cdot\text{mol}^{-1}$ )<sup>12</sup>, which, in its turn, can decompose into Cl monofluoride and  $\text{O}_2$ <sup>34</sup> according to the reaction

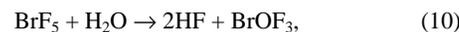


and of the structurally nonrigid complex (an adduct) of  $\text{ClF}_3\cdot\text{HF}$ .

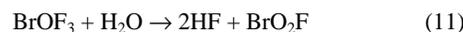
In the process of Br trifluoride hydrolysis, the HF, HBr,  $\text{Br}_2$ , and  $\text{O}_2$  molecules are produced. As in the case with the Cl fluorides, a possibility exists of forming of an unstable BrOF compound which then decomposes following the scheme (9) into BrF and  $\text{O}_2$ .

Reaction of  $\text{BrF}_5$  with water proceeds similarly to that according to scheme (6) with the formation of

bromylfluoride with the consequent hydrolysis of the latter according to scheme (7). But, unlike  $\text{ClF}_5$  hydrolysis, the chemically active  $\text{BrOF}_3$  can play the role of intermediate product in the interaction between  $\text{BrF}_5$  and water



which hydrolyzes much faster than  $\text{BrF}_5$



and therefore it is not normally found among the products of  $\text{BrF}_5$  hydrolysis.<sup>32</sup>

### 3. Results and discussion

#### $\text{ClF}_3$ and $\text{BrF}_3$ molecules

The  $\text{ClF}_3$  and  $\text{BrF}_3$  molecules (point symmetry  $\text{C}_{2v}$ ) have six normal nondegenerate vibrations of the symmetry types

$$\Gamma_{\text{vib}} = 3A_1 + 2B_1 + B_2, \quad (12)$$

active both in the IR and Raman spectra.

**Table 2. Experimental frequencies ( $\text{cm}^{-1}$ ) and their interpretation in the IR-spectra for  $\text{XF}_3$  ( $\text{X} = \text{Cl}, \text{Br}$ ) molecules in gas phase ( $T = 293 \text{ K}$ ) and in Kr ( $L\text{Kr}$ ,  $T = 130 \text{ K}$ ) and Xe ( $L\text{Xe}$ ,  $T = 180 \text{ K}$ ) cryogenic solutions**

$\text{ClF}_3$			$\text{BrF}_3$			Vibration type and interpretation	
Solution in <i>LKr</i>	Gas	Gas Ref. 35	Solution in <i>LXe</i>	Gas	Gas Ref. 36		
1959	–	–	1865	–	–	$2\nu_1 + \nu_2 (\hat{A}_1)$	
1860	–	–	1626	–	–	$\nu_1 + \nu_4 + \nu_5 (\hat{A}_1)$	
1793	–	–	1571	–	–	$2\nu_1 + \nu_3 (\hat{A}_1)$	
1761	–	–	1516	–	–	$\nu_1 + \nu_3 + \nu_4 (\hat{A}_1)$	
1749	–	–	–	–	–		
1618	–	–	1504	–	–	$\nu_2 + \nu_4 + \nu_5 (\hat{A}_1)$	
1551	1517	–	–	–	–	$\nu_2 + \nu_4 + \nu_6 (\hat{A}_2)$	
1519	1541	–	1393	–	–	$\nu_2 + \nu_3 + \nu_4 (\hat{A}_1)$	
1493	1501	1488	1335	1342	1340	$2\nu_1 (\hat{A}_1)$	
1486	1490	1466	1329	1334			
1455	1466	1466	1281	1290	1287	$\nu_1 + \nu_4 (\hat{A}_1)$	
1437	1450	1451	1274	1282			
1330	1343	1338	–	–	–	$2\nu_3 + \nu_4 (\hat{A}_1)$	
1261	1274	1273	1209	1217	–	$\nu_1 + \nu_2 (\hat{A}_1)$	
1214	1225	1223	1156	1165	1162	$\nu_2 + \nu_4 (\hat{A}_1)$	
1205	1213		1149				
1050	–	–	–	–	–	$2\nu_3 + \nu_5 (\hat{A}_1)$	
1015	1024	1022	901	–	–	$\nu_3 + \nu_4 (\hat{A}_1)$	
948	958	957	884	–	–	$\nu_2 + \nu_5 (\hat{A}_1)$	
839	850	845	706	–	–	$\nu_2 + \nu_3 (\hat{A}_1)$ or $2\nu_5 (\hat{A}_1)$	
748	756	761	677	683	682	$\nu_1 (\hat{A}_1), \nu (\text{X–F}_{\text{eq}})$	
735	739	741	667	670	668		
	712	711					
	706	709	704				
	696	704	701	615	619	621	
	691	700	698	607	615	614	$\nu_4 (\hat{A}_1),$
	684	697	694	598	605	604	$\nu_{\text{as}} (\text{X–F}_{\text{ax}})$
	674	693	691				
	691						
	647	653	–	–	–	–	$2\nu_3 (\hat{A}_1)$
	527	525	535	540	558	557	$\nu_2 (\hat{A}_1),$
	510	516	518	533	547	547	$\nu_5 (\text{X–F}_{\text{ax}})$
				354	360	359	
				335	352	350	$\nu_5 (B_1),$
					340	342	$\delta (\text{X–F}_{\text{eq}})$ on plane

362	364	364	-	-	242	$\nu_6(B_2)$ , $\delta(X-F_{eq})$ off plane
327	331	332	-	-	242	$\nu_3(A_1)$ ,
315	318	319	-	-		$\delta(X-F_{ax})$

Note:  $\nu$  is for the valence vibration,  $\delta$  is for the deformation one; "s" denotes symmetric and "as" is the antisymmetric vibration.

The gas-phase  $XF_3$  vibrational spectra ( $X = Cl, Br$ ) were studied in Refs. 35 and 36; those in condensed state and under conditions of matrix confinement – in Refs. 37–40. The authors of these papers have performed an assignment of the  $ClF_3$  and  $BrF_3$  fundamental frequencies and defined a set of valence force constants. Attempts to interpret some second-order transition bands in the IR spectra of gaseous  $ClF_3$  and  $BrF_3$  were made in Refs. 35 and 36. Table 2 lists the frequency values of the IR absorption bands of the gas-phase  $ClF_3$  and  $BrF_3$  as well as in Kr and Xe cryogenic solutions that we have measured ourselves. Those taken from Refs. 35 and 36 are presented for a comparison.

A portion of IR spectrum for gas-phase  $ClF_3$  and that in Kr cryogenic solution for the frequency range of vibration of  $(Cl-F)_{ax}(\nu_4)$  bond is shown in Fig. 2.

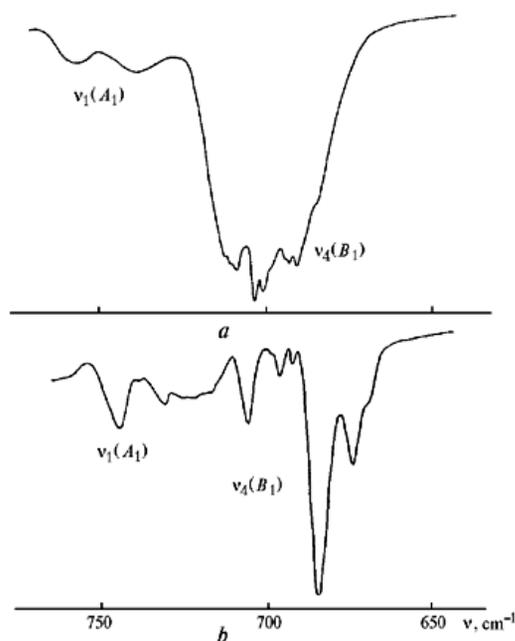


Fig. 2. A fraction of the IR absorption spectrum of  $ClF_3$  molecule in the gas phase (a) and Kr cryogenic solution (b) near the  $\nu_4(B_1)$  mode.

As seen from Table 2, we have managed to record and interpret more than 30 ( $ClF_3$ ) and 20 ( $BrF_3$ ) vibrational bands in the frequency range from 2000 down to 300  $cm^{-1}$  including the third-order transition bands. It is noteworthy that the shapes of asymmetrical vibration band of the axial bond  $\nu_4(B_1)$  of the gas-phase  $ClF_3$  and  $BrF_3$  are a superposition of several overlapping bands with the frequencies 712, 709, 704, 700, 697, 693, and 691  $cm^{-1}$  ( $ClF_3$ ) and 619, 615, and 605  $cm^{-1}$  ( $BrF_3$ ). This fact agrees well with the data from Refs. 35 and 36, the authors of which also observed a complicated structure of  $\nu_4$  band

consisting of several bands with the frequencies 711, 704, 701, 698, 694, and 691  $cm^{-1}$  (in  $ClF_3$ ) and 621, 614, and 604  $cm^{-1}$  (in  $BrF_3$ ). The complicated structure of the  $\nu_4$  band is, in our opinion, due to Coriolis interaction typical for T-shape molecules of the  $C_{2v}$  symmetry.<sup>41</sup>

For the T-shape  $XY_3$  molecules, three types of Coriolis interaction among the fundamental vibrations are possible:  $(A_1, B_1)$ ,  $(A_1, B_2)$ , and  $(B_1, B_2)$ . The latter interaction type is a consequence of the fact that the  $XY_3$  ( $C_{2v}$ ) molecules do not have fundamental vibrations of  $A_2$  symmetry. The rotation of a molecule about this symmetry axis results in the  $\nu_6(B_2)$  vibration excited by the Coriolis force arising at  $\nu_5(B_1)$  vibration. Since the frequencies of these vibrations are close to each other, a noticeable interaction arises between these vibrational states. The  $\nu_3(A_1)$  and  $\nu_6(B_2)$  vibrations that have close frequencies can also interact rather strongly on their rotation about the axis of central moment of inertia. The strongest interaction, in our opinion, can take place between  $\nu_1(A_1)$  and  $\nu_4(B_1)$  vibrations that have close frequencies at rotation about the axis of maximum moment of inertia.

In contrast to the gas phase, in cryogenic solutions sufficiently well resolved bands at the frequencies of 706, 696, 691, 684, 674 and 615, 607, 598  $cm^{-1}$  and the intensity ratios of 0.25:0.11:0.07:1.0:0.35 and 0.77:1.0:0.46, respectively, are observed instead of complicated IR absorption spectra of  $ClF_3$  and  $BrF_3$  near the  $\nu_4(B_1)$  mode. The splitting observed in the  $\nu_1$ ,  $\nu_2$ , and  $\nu_5$  bands, as in the  $\nu_4$  band, is also due to the Coriolis interaction. It should be noted that the  $\nu_4$  band strength in  $ClF_3$  and  $BrF_3$  IR spectra is anomalously high (by more than an order of magnitude) as compared with the  $\nu_1$  band strength and about two orders of magnitude higher than the intensity of other fundamental bands. This fact is evidently characteristic of  $XY_3$  ( $C_{2v}$ ) molecules of the T-shape structure.

As in the case with other polyatomic molecules,<sup>13–15</sup> the gas-to-cryogenic solution transition is accompanied by a low-frequency shift of  $ClF_3$  and  $BrF_3$  vibrational bands. Among the fundamental bands the maximum shift is characteristic of the valence vibration bands. At the same time such a shift of the deformation vibrational bands is almost a half as low. The shift of combination vibrational bands and overtones achieves several tens of wavenumbers. The additivity that approximately holds allows one to hope that the values of unharmonicity constants, calculated for  $ClF_3$  and  $BrF_3$  solutions in liquid noble gases, will be close to the corresponding values of  $X_{ik}$  in the gas phase.

Taking into account these circumstances and based on the obtained spectroscopic evidences of the frequency position of a series of combination bands and overtones, we have computed the unharmonicity constants for some  $ClF_3$  and  $BrF_3$  vibrations:  $X_{33} = -7.0$   $cm^{-1}$ ,  $X_{11} = -5.0$   $cm^{-1}$ ,  $X_{25} = -9.0$   $cm^{-1}$  ( $ClF_3$ ) and  $X_{11} = -6.0$   $cm^{-1}$ ,  $X_{25} = -10.0$   $cm^{-1}$  ( $BrF_3$ ). Evaluation of  $X_{ik}$  for other vibrations, in particular,  $X_{4k}$  or  $X_{i4}$  ( $i, k = 1, 2, \dots, 6$ ) faces some difficulties because of the  $\nu_4$  band splitting due to the Coriolis interaction.

### $ClF_5$ and $BrF_5$ molecules

The pentafluorides of Cl and Br belong to  $C_{4v}$  point symmetry group and are characterized by nine normal vibrations of the symmetry types

$$\Gamma_{vib} = 3A_1 + 2B_1 + B_2 + 3E. \quad (13)$$

In the IR absorption spectrum of these molecules only vibrations of  $A_1(\nu_1, \nu_2, \nu_3)$  and  $E(\nu_7, \nu_8, \nu_9)$  symmetry are active, in Raman spectrum – all nine vibrations are active.

The vibrational spectra of  $ClF_5$  and  $BrF_5$  in gas and liquid phases were studied in Refs. 37, 42–44. The authors of Refs. 40, 45, and 46 have obtained evidences on spectra of these molecules isolated in matrices of the inert gases. In the above cited works, the fundamental bands of  $ClF_5$  and  $BrF_5$  were interpreted<sup>42,44</sup> and the values of vibration amplitudes and Coriolis constants computed. Isotopic frequency shifts of some vibrational bands were determined in Refs. 45 and 46.

The frequencies, relative intensities, and identification of the observed IR absorption bands of these molecules in the gas phase and in cryogenic solutions in Kr and Xe are presented in Tables 3 and 4. The frequencies of IR absorption bands for gas-phase  $ClF_5$  and  $BrF_5$  from Refs. 42 and 43 are also presented in these tables.

A portion of IR spectrum of  $ClF_5$  cryogenic solution in Xe within the region of the second- and third-order transitions is depicted in Fig. 3.

It follows from the data given in Table 3 that we have managed to record more than 50 ( $ClF_5$ ) and 40 ( $BrF_5$ ) vibrational bands in the IR absorption spectrum of  $ClF_5$  and  $BrF_5$  cryogenic solutions in liquid Xe in the frequency range from 2300 to 200  $cm^{-1}$ . At the same time, the IR spectra of their solutions in liquid Kr are characterized by smaller number (32 for  $ClF_5$  and 26 for  $BrF_5$ ) of absorption bands within the ranges 1700–300 and 1400–215  $cm^{-1}$ , respectively, what can be attributed to worse solubility of these interhalides in liquid Kr as compared with liquid Xe.

Similarly to gas-phase absorption spectra of  $ClF_5$  and  $BrF_5$ , the bands of the  $\nu_1, \nu_2,$  and  $\nu_3$  fundamental vibrations (symmetry  $A_1$ ) as well as  $\nu_7, \nu_8,$  and  $\nu_9$  bands (symmetry  $E$ ), allowed by the selection rules for  $C_{4v}$ -configurations, are observed in the spectra of cryogenic solutions of these species in liquid Xe within the above-mentioned frequency ranges.<sup>47</sup> No serious problems arise in assigning of the observed fundamental bands of  $BrF_5$  both in gas phase and cryogenic solutions. At the same time, in the case of  $BrF_5$  only three fundamental vibrations with the frequencies of 718.7, 537.0, 516.0, and 476.5  $cm^{-1}$  (liquid Xe); 720.0, 540.0, 518.0, 476.5  $cm^{-1}$  (liquid Kr); and 731.8, 541.0  $cm^{-1}$  (gas phase) can be interpreted unambiguously. Group identification of the fundamental vibration bands in the frequency ranges of 710 and 480  $cm^{-1}$  was performed. As to the combination vibrations and overtones of  $ClF_5$  and  $BrF_5$ , only a half of them can be interpreted. For other bands of the second- and third-order transitions only group interpretation is possible. Note that the above bands may be assigned to some transitions only on the basis of Raman spectra of the above species dissolved in liquid noble gases.

**Table 3. Parameters of absorption bands ( $cm^{-1}$ ) for  $ClF_5$  molecules in the gas phase and in cryogenic solutions in Xe and Kr (LXe and LKr, respectively)**

Solution in LXe	Solution in LKr	Gas	Gas Ref. 42	$A_{rel}$	Vibration type and interpretation
1	2	3	4	5	6
2251	–	2199	2202	0.3	$3\nu_7 (E)$
2188				0.8	$\nu_1 + 2\nu_7 (A_1)$ $2\nu_7 + \nu_8 + \nu_9 (E)$
1932	–	1938	1940	0.2	$\nu_2 + 2\nu_7 (A_1)$
1927					

1880	–	–	–	–	–	–	–	–	–	–
1859	–	–	1871	–	0.8					$\nu_1 + \nu_6 + \nu_7 (E)$
1854	–	–	–	–	–	–	–	–	–	–
1811	–	–	1825	1828	0.3					$2\nu_2 + \nu_7 (\hat{A})$
1786	–	–	1794	–	0.2					$\nu_1 + 2\nu_2 (A_1)$
1710	1712	1706	1704	0.3						$\nu_2 + \nu_3 + \nu_7 (E)$
1701	1704	–	–	–	–					$2\nu_3 + \nu_7 (\hat{A})$ $2\nu_7 + \nu_9 (E)$
1684	1687	–	–	0.2						$\nu_3 + \nu_7 + \nu_8 (\hat{A})$ $2\nu_3 + \nu_7 (\hat{A}) ?$
1492	1494	1517	1500	1.0						$\nu_3 + \nu_7 + \nu_9 (\hat{A}_1 + \hat{A}_1 + \hat{A}_2)$
1434	1437	1449	1444	10						$2\nu_7 (\hat{A})$ <sup>35</sup> Cl
1411	1412	–	–	3.5						$\nu_1 + \nu_7 (\hat{A})$ $2\nu_7 (\hat{A})$ <sup>37</sup> Cl
1306	1307	1316	1322	10						$\nu_7 + 2\nu_9 (\hat{A})$
1290	1291	–	–	–	–					–
1255	1256	1260	1274	15						$\nu_2 + \nu_7 (\hat{A})$
1242	1244	1249	–	–	–					$\nu_1 + \nu_2 (\hat{A}_1)$ $\nu_7 + \nu_8 (\hat{A})$ $\nu_1 + \nu_3 (\hat{A}_1)$
1199	1203	1213	1220	15						$\nu_3 + \nu_7 (\hat{A})$ $\nu_4 + \nu_7 (\hat{A})$ $\nu_1 + \nu_8 (\hat{A})$
1185	1186	–	–	–	–					$\nu_7 + \nu_8 (\hat{A})$
1199	1203	1213	1220	15						$\nu_1 + \nu_3 (\hat{A}_1)$ $\nu_3 + \nu_7 (\hat{A})$ $\nu_4 + \nu_7 (\hat{A})$ $\nu_1 + \nu_8 (\hat{A})$
1185	1186	–	–	–	–					$2\nu_2 (\hat{A}_1)$
1076	1077	1084	1088	0.1						$\nu_5 + \nu_7 (\hat{A})$
1054	1056	1060	–	2.0						$\nu_7 + \nu_9 (\hat{A})$
1017	1020	1023	1028	1.0						$\nu_2 + \nu_8 (\hat{A})$ $\nu_2 + \nu_3 (\hat{A}_1)$
1014	–	–	–	–	–					$\nu_1 + \nu_9 (\hat{A})$
998	–	–	–	0.4						$\nu_3 + \nu_4 (\hat{A}_1)$
988	–	–	–	0.2						$2\nu_3 (\hat{A}_1)$
977	980	981	981	3.0						$\nu_3 + \nu_8 (\hat{A})$
972	–	–	–	–	–					$\nu_3 + \nu_8 (\hat{A})$
875	876	978	–	0.5						$\nu_3 + \nu_6 (\hat{A}_1 + \hat{A}_1 + \hat{A}_2)$
835	837	842	840	3.0						$\nu_2 + \nu_9 (\hat{A})$
782	784	785	786	–	–					$\nu_3 + \nu_9 (\hat{A})$
744	–	–	–	60						$\nu_8 + \nu_9 (\hat{A})$
737	–	–	–	–	–					$\nu_4 + \nu_9 (\hat{A})$
718.7	720.0	731.8	732	1000						$\nu_7 (\hat{A}), \nu_{as} (^{35}Cl-F)_{ax}$
713.5	–	–	–	–	–					$\nu_1 (\hat{A}_1), \nu_s (^{35}Cl-F)_{eq}$
710.0	708.9	–	–	390						$\nu_1 (\hat{A}_1), \nu_s (^{37}Cl-F)_{eq}$
707.5	–	–	–	–	–					$\nu_7 (\hat{A}), \nu_{as} (^{37}Cl-F)_{ax}$
617	618	–	–	0.5						$\nu_5 + \nu_9 (\hat{A})$
607	608	–	–	–	–					–
597	601	–	–	–	–					–
587	590	608	598	1.0						$2\nu_9 (\hat{A}_1)$
584	–	–	–	–	–					–
537	540	541	541	6.0						$\nu_2 (\hat{A}_1), \nu_s (Cl-F)_{ax}$
516	518	–	–	–	–					–
491.5	494	–	–	70						$\nu_3 (\hat{A}_1),$ $\delta_s (F_{ax} - ^{35}Cl - F_{ax})$
481	482	485	486	180						$\nu_3 (\hat{A}_1),$ $\delta_s (F_{ax} - ^{37}Cl - F_{ax})$ $\nu_8 (\hat{A}), \delta_{as} (F_{eq} - ^{35}Cl - F_{ax})$ off plane
476	477	–	–	45						$\nu_8 (\hat{A}), \delta_{as} (F_{eq} - ^{37}Cl - F_{ax})$ off plane
299	301	303	302	200						$\nu_9 (\hat{A}), \delta_{as} (F_{ax} - Cl - F_{ax})$ on plane



agrees with that (70) from Ref. 44, but the corresponding value of  $A_8$  differs and equals to 20.

Our estimates of integral absorption coefficients within the most intense  $\nu_7(E)$  band of  $^{35}\text{ClF}_5$  and  $\text{BrF}_5$  placed into the medium of liquid noble gases gave sufficiently large values and equal to  $(370 \pm 50) \cdot 10^{-8}$  and  $(325 \pm 60) \cdot 10^{-8} \text{ cm}^2 \cdot \text{molec}^{-1} \cdot \text{s}^{-1}$ , respectively.

A comparison of frequencies of fundamental vibrations in gas-phase  $\text{ClF}_5$  and  $\text{BrF}_5$  with these in spectra of their cryogenic solutions in Kr and Xe has shown that the band of antisymmetric vibration  $\nu_7(E)$  experiences the maximum low-frequency shift. The shift values are 11.8 and  $13.1 \text{ cm}^{-1}$  ( $\text{ClF}_5$ ); 8.0 and  $11.0 \text{ cm}^{-1}$  ( $\text{BrF}_5$ ) for liquid Kr and Xe, respectively. The shift for  $\nu_2$  band is somewhat smaller: 1.0 and  $4.0 \text{ cm}^{-1}$  ( $\text{ClF}_5$ ); 4.0 and  $6.0 \text{ cm}^{-1}$  ( $\text{BrF}_5$ ); the shifts of  $\nu_1$ ,  $\nu_3$ ,  $\nu_8$ , and  $\nu_9$  bands of  $\text{BrF}_5$  are 3.0, 3.0, 2.0, and  $2.0 \text{ cm}^{-1}$  (in liquid Kr) and 6.0, 5.0, 4.0, and  $3.0 \text{ cm}^{-1}$  (in liquid Xe), respectively. Almost all uniquely interpreted components of the  $\nu_7$  band undergo strong shift (up to  $25 \text{ cm}^{-1}$ ), while combination bands and overtones with the participation of other quanta undergo somewhat smaller shifts. The frequency shifts of other  $\text{ClF}_5$  fundamental bands as well as these of transitions of higher orders are an open question due to the lack of uniqueness in their assigning to one or another vibrational transition. Like in the case with  $\text{ClF}_5$  and  $\text{BrF}_5$ , the anharmonicity constants  $X_{ik}$  ( $\text{cm}^{-1}$ ) for some  $\text{ClF}_5$  and  $\text{BrF}_5$  vibrations were calculated based on the frequency values obtained for some combination vibrations and overtones.

$$X_{22} = -3; \quad X_{33} = -6; \quad X_{77} = -3.4;$$

$$X_{12} = -5; \quad X_{27} \cong -1 \quad (\text{ClF}_5); \quad (14)$$

$$X_{12} = -10; \quad X_{33} = -8; \quad X_{18} = -9; \quad X_{78} = -2;$$

$$X_{38} = -12; \quad X_{39} = -2; \quad X_{99} = -3 \quad (\text{BrF}_5). \quad (15)$$

There occur difficulties in the  $X_{ik}$  determination for other  $\text{ClF}_5$  and  $\text{BrF}_5$  vibrations because of ambiguity in their assigning to a definite vibrational transition.

The values of isotopic shifts  $\Delta\nu_i$  obtained for some  $\text{ClF}_5$  vibrational bands are the following:

$$\Delta\nu_7 = 11.2, \quad \Delta\nu_3 = 10.5, \quad \Delta\nu_1 = 3.5, \quad \Delta\nu_8 = 4.5 \text{ cm}^{-1}. \quad (16)$$

Note that isotopic shifts of the  $\text{ClF}_5$  fundamental vibrations were experimentally measured and reported in Refs. 45 and 46, the authors of which studied the  $\text{ClF}_5$  IR spectra under conditions of matrix isolation. They have obtained the following values:

$$\Delta\nu_7 = 12.8, \quad \Delta\nu_3 = 10.0, \quad \text{and} \quad \Delta\nu_8 = 3.3 \quad \text{Ref. 46;}$$

$$\Delta\nu_7 = 12.7, \quad \Delta\nu_3 = 3.5, \quad \text{and} \quad \Delta\nu_1 = 4.5 \quad \text{Ref. 45.} \quad (17)$$

As the presented data show, the  $\Delta\nu_i$  values obtained by us rather well agree with the corresponding values from Ref. 46 as well as with  $\Delta\nu_1$  and  $\Delta\nu_7$  values from Ref. 45. At the same time, the magnitude of  $\Delta\nu_3$  from Ref. 45 is almost three times less than ours and that from Ref. 46. Possibly, this is due to spectral effects of matrix splitting.

Detailed analysis of the spectroscopic data obtained in this work for molecules  $\text{ClF}_5$  and  $\text{BrF}_5$  has pointed to some anomalies in relations of absorption band intensities, fundamental force constants, interaction constants, and so on.

It is well known, that calculation of the vibrational bands intensities in the IR spectra of polyatomic fluorine-containing molecules is usually based on empirical model of fluorine atom polar tensors of the form<sup>48</sup>

$$D_x^F = \begin{pmatrix} \partial\delta_x/\partial x_F & \partial\delta_x/\partial y_F & \partial\delta_x/\partial z_F \\ \partial\delta_y/\partial x_F & \partial\delta_y/\partial y_F & \partial\delta_y/\partial z_F \\ \partial\delta_z/\partial x_F & \partial\delta_z/\partial y_F & \partial\delta_z/\partial z_F \end{pmatrix}, \quad (18)$$

where  $p_i$  are the components of dipole moment transformed upon representation of the corresponding Cartesian displacement;  $x$ ,  $y$ , and  $z$  are spatially fixed coordinates of the fluorine atom.

The polar tensor was slightly varied from one molecule to another (Refs. 44 and 48), and for the umbrella-shaped molecules of  $C_{4v}$  symmetry (including pentafluoride halides) it can be written<sup>44</sup> as

$$P_{ax}^F = \begin{pmatrix} 0.21 & 0 & 0 \\ 0 & 0.21 & 0 \\ 0 & 0 & 0.90 \end{pmatrix} e \quad (19)$$

– for an axial  $F$  atom and

$$P_{eq}^F = \begin{pmatrix} 0.25 & 0 & 0 \\ 0 & 0.25 & 0 \\ 0 & 0 & 1.00 \end{pmatrix} e \quad (20)$$

– for an equatorial  $F$  atom.

Here the diagonal elements are the derivatives of the dipole moment corresponding to  $F$  atom shift along two directions (perpendicular and along the bond).

Our analysis of the absorption IR spectra for five-coordinate compounds in cryogenic solutions of noble gases has shown that the observed band intensities of the valence vibrations for  $\text{ClF}_5$  and  $\text{BrF}_5$  insignificantly correlate with the well-known relation for molecules of  $C_{4v}$  symmetry following from the model of local oscillations<sup>49</sup>

$$[I(\nu_1) + I(\nu_2)] : [I(\nu_7)] \cong 1:4. \quad (21)$$

The calculations made in Ref. 44 for  $\text{ClF}_5$  and  $\text{BrF}_5$  molecules give the ratios 1:3.3 and 1:3.74, and some difference with the proportion (21) is due, in the opinion of the authors of Ref. 44, to “interference” of the deformation coordinates. This intensity ratio determined in Ref. 45 for  $\text{ClF}_5$  is 1:17, whereas our data give 1:6.4 and 1:30 for  $\text{ClF}_5$  and  $\text{BrF}_5$ , respectively. On substitution  $I(\nu_3)$  into (21) the ratios become 1:11.1 ( $\text{ClF}_5$ ) and 1:13.3 ( $\text{BrF}_5$ ); the former of these values well agrees with the data from Ref. 45 (1:11.0). The authors of Ref. 44 came to a conclusion that different values of the ratio (21) for calculated and experimentally obtained intensities for  $\text{ClF}_5$  and  $\text{BrF}_5$  fundamental absorption bands are first of all associated with the incorrectness of the force field model for these molecules. The authors of Refs. 30, 44, and 45 have noted that application of the polar tensors model to description of the  $X-F_{ax}$  and  $X-F_{eq}$  bonds ( $X = \text{Cl}, \text{Br}$ ) is not exactly correct, because the effective charge on  $F_{ax}$  is noticeably less than on  $F_{eq}$ . The calculation of dipole moment derivatives for  $\text{ClF}_5$  made in Ref. 45 as well as our estimates<sup>49</sup> have shown that in moving  $F_{ax}$  and  $F_{eq}$  along the bond, the difference between these derivatives is almost an order of magnitude ( $\cong -0.1e$  and  $\cong -1.0e$ ), whereas the dipole moment derivatives at  $F_{eq}$  displacement

perpendicular to the bond are comparable in magnitude ( $\cong +0.26e$  and  $\cong +0.14e$ ). For  $\text{BrF}_5$ , the dipole moment derivatives have not been calculated, but we estimate the situation with their magnitudes in  $F_{\text{ax}}$  and  $F_{\text{eq}}$  shifts along the bond as similar to the case with  $\text{ClF}_5$ . Therefore, we can argue in favor of the fact that  $\text{X-F}_{\text{ax}}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) bond by its electrooptical parameters significantly differs both from equatorial bond and from other bonds in five- or six-coordinate fluorides ( $\text{PF}_5$ ,  $\text{SF}_5$ , and others), for which the tensor (18) was successfully used. Such a conclusion agrees with the results of quantum-chemical calculations for electron-excessive interhalides<sup>12,50,51</sup> and suggests that the bonds in  $\text{XF}_5$  ( $\text{X} = \text{Cl}, \text{Br}$ ) molecules can be classified into two categories:

- the bonds to which both the  $s$ - and  $p$ -orbitals of the central atom ( $\text{X-F}_{\text{ax}}$  bond) contribute;
- the bonds with more ions along linear groups  $\text{F-X-F}$  formed exclusively by  $p$ -orbitals of the central atom ( $\text{X-F}_{\text{eq}}$  bonds).

The  $\text{ClF}_5$  and  $\text{BrF}_5$  electrooptical parameters can be discussed in a more detail only after reliable determination of their valence-force field, because we still have no final answer to this question. Various simplifying suppositions used in finding the force parameters have a particularly strong effect on the off-diagonal elements of the  $F$ -matrix.<sup>50</sup> The difference is observed not only in  $F_{ij}$  magnitudes, but also in their signs.<sup>12,30,46</sup> A model of infrared intensities for  $\text{ClF}_5$  and  $\text{BrF}_5$  should take into account both the characteristic differences in  $\text{X-F}_{\text{ax}}$  and  $\text{X-F}_{\text{eq}}$  bonds and the contributions from unbounded electron pair and from nonrigid intramolecular regroupings. In the case of nonrigid regroupings in  $\text{ClF}_5$  and  $\text{BrF}_5$ , a fast axial-equatorial exchange of  $\text{F}$ -ligands can take place, what is clearly demonstrated by the NMR-spectra.<sup>52</sup>

In the case of five-coordinate bonds, the most probable mechanisms of intramolecular regroupings can be pseudorotations via configuration of trigonal bipyramid (TBP) and the tourniquet mechanism of  $\text{F}$  atoms exchange.<sup>53</sup> So, following the estimates made in Ref. 50, a barrier for pseudorotation in  $\text{ClF}_5$  via TBP-configuration ( $D_{3h}$ ) is  $\cong 80 \text{ kcal}\cdot\text{mol}^{-1}$ , i.e., this mechanism of intramolecular regroupings may be eliminated from consideration as energetically disadvantageous. The tourniquet mechanism of  $\text{F}$  atoms exchange in pentafluoride halides was also treated<sup>50</sup> and, similarly to the above pseudorotation mechanism, was excluded from consideration based on corresponding calculations by Hartree-Fock method, which were made not for five-coordinate  $\text{XF}_5$  molecules, but for  $\text{SH}_6$  and  $\text{SF}_6$  molecules with two-exponent  $sp$ -basis.<sup>51</sup> At the same time, the authors of Ref. 50 pay attention to a noticeable role of the polarization  $d$ -functions of the central atom and effects of electron correlation, in finding the barriers for intramolecular regroupings in fluorides of the elements from the IIIrd period. Our estimates<sup>30,54</sup> have shown that if more complete bases are used and the effects of electron correlation are taken into account, a moderate height of the barrier for regrouping by tourniquet mechanism can be expected, which case, in our opinion, is most probable for  $\text{ClF}_5$  and  $\text{BrF}_5$ . But the lack of direct *ab initio* calculations for the tourniquet mechanism potential surface as for other possible mechanisms of the ligands exchange in  $\text{ClF}_5$  and

$\text{BrF}_5$ , as well as unavailability of reliable valence-force field for these compounds make the question on the contribution of nonrigid intramolecular regroupings to the formation of  $\text{ClF}_5$  and  $\text{BrF}_5$  infrared intensities still open, thus demonstrating the necessity of further study using not only spectroscopic but also the up-to-date physical methods of chemistry.

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