Vibrational spectroscopy of complex compounds of gold pentafluoride

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IR and Raman spectra of $X^+AuF_6^-$ (X = ClF_2, ClO_2, $ClOF_2$, ClF_4, ClF_6) were studied. The vibration frequencies of these compounds in the solid phase and in solutions in anhydrous HF were assigned. Peculiar features of the vibrational spectra of solid $X^+AuF_6^-$, associated both with structural transformations of cations and anions in the crystal lattice field and cation—anion interactions and also with the Jahn—Teller effect, Fermi resonance, non-rigid intramolecular rearrangements., *etc.*, were discussed.

Key words: vibrational spectrum, complex compound, Lewis acid, bond vibration frequency, intensity of spectral line, cation—anion interactions, hexafluoroaurate ion.

Of the higher fluorides of the third row transition metals, AuF_5 is one of the least studied.[1] This compound was first synthesized[2] as the complex $2XeF_6 \cdot AuF_5$. Unlike other transition metal higher fluorides, gold pentafluoride possesses high chemical reactivity, which is manifested in that it oxidizes elementary xenon at ambient temperature to at least XeF_4.[3] Meanwhile, the average energy of the Au—F bond in AuF_5 (~54 kcal mol^{-1}) differs only slightly from the corresponding value in AuF_3 (~61 kcal mol^{-1}).[1,4]

This communication is devoted to the study of vibrational spectra and structural features of the complexes $X^+AuF_6^-$ (X = ClF_2^+, ClO_2^+, $ClOF_2^+$, ClF_4^+, and ClF_6^+).

Experimental

The complexes of AuF_5 were synthesized by a previously described procedure.[5,6] The IR spectra of solid samples, which were placed as finely dispersed powders in an air-proof Teflon mounting between plates of AgCl single crystals, were studied in the 400—2000 cm^{-1} frequency range using Specord IR-75 and Perkin—Elmer-325 two-beam spectrophotometers (spectral slit width 2.5—3.0 cm^{-1}). Raman spectra were recorded using an RTI-30 (Dilor) Raman spectrometer with a triple monochromator. The spectral slit width of the spectrometer was maintained constant (3.7 cm^{-1} and 2.0 cm^{-1} for solid samples and solutions in HF, respectively). An LGN-503 Ar^+ laser (500 mW) with an exciting line at 488 nm and an LGN-104 He—Ne laser (50 mW) with a radiation wavelength of 632.8 nm were used as the excitation sources. Samples were placed in transparent tubes made of the fluoroplastic 4MB, and the sample temperature was maintained constant (292± 2 K) using a water thermostat. The accuracy of determination of AuF_5 compounds in HF was 5—10%. HF was thoroughly purified and dried. The extent of drying was checked by analyzing the IR absorption bands in the region of stretching vibrations of water using a cell with a controlled thickness specially designed for corrosive liquid media. All operations associated with sample preparation were carried out under dry argon. The accuracy of determination of the absorption maxima in the IR spectra and lines in the Raman spectra was at least 2 and 1 cm^{-1}, respectively.

Results and Discussion

The complex compounds of AuF_5 have mostly been studied[2,4—9] by Raman spectroscopy. This method was used predominantly because the selection rules allow nearly identical sets of active vibrations to be observed in the IR and Raman spectra for molecules with relatively low symmetry ($D_{\infty h}$, C_{2v}, *etc.*). When molecules of a studied compound possess a higher symmetry (O_h, T_d, *etc.*), the number of Raman-active vibrations is 1.5—2-fold greater than the number of IR-active vibrations.

The molecules of transition metal pentahalides, unlike five-coordinate interhalogens (tetragonal pyramid, C_{4v}), belong as a rule to the D_{3h} point group of symmetry (trigonal bipyramid).[10] The results of studies of the AuF_5 structure by various physical methods (vibrational spectroscopy,[2,4—9] electron diffraction,[11] Mössbauer spectroscopy,[9] and XRD of AuF_5 powder[2,4,12]) available now do not answer unambiguously the question of what is the structure of this compound both in the gaseous and condensed phases. It follows from the whole set of these data that in the gas phase at ~500 K, AuF_5 mainly consists of Au_2F_{10} (D_{2h}) dimers and Au_3F_{15} (D_{3h}) trimers. The crystal structure of AuF_5 is built apparently of polymer chains twisted into a helix (to give a sixfold screw axis[12]) and formed by distorted Au^VF_6 octahedra connected to one another by bridging fluorine atoms located in the *cis*-positions.[13]

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Unlike the AuF_5 structure, the structure of the AuF_6^- anion in its complexes does not arouse serious doubts. The Mössbauer spectrum[9] of $KrF^+AuF_6^-$ exhibits one line with an isomeric shift of ~2.3 mm s^{-1}, indicating a high symmetry of the anion. This is also confirmed by the results[2] of X-ray diffraction analysis of $Xe_2F_{11}^+AuF_6^-$. The frequencies recorded in the IR and Raman spectra[2,4,7,8] of hexafluoroaruate ions can be assigned to vibrations of an O_h structure, characterized by six normal modes with the following types of symmetry:

$$\Gamma_{vib} = A_{1g}\ (\text{Raman}) + E_g\ (\text{Raman}) + 2F_{1u}\ (\text{IR}) + F_{2g}\ (\text{Raman}) + F_{2u}\ (\text{IA});$$

three vibrations (ν_1, ν_2, ν_5) are active only in the Raman spectra, two other modes (ν_3, ν_4) are active only in the IR spectrum, and one (ν_6) is inactive (IA) in both types of spectra. According to the selection rules,[10] the vast majority of octahedral hexahalides[10,14] XY_6 are characterized by a definite order of arrangement of stretching ($\nu_1 < \nu_3 > \nu_2$) and deformation frequencies. Therefore, the lines at 600, 530, and 230 cm^{-1} found in the Raman spectra of hexafluoroaruate ions[2,4,7,8] were assigned to $\nu_1(A_{1g})$, $\nu_2(E_g)$, and $\nu_5(F_{2g})$, respectively, whilst the bands at 640 and 260 cm^{-1} in the IR spectra were attributed to $\nu_3(F_{1u})$ and $\nu_4(F_{2u})$ modes, respectively. Regarding the $\nu_6(F_{2u})$ vibration, which is inactive in both types of spectra, according to our estimates,[14] its frequency is ~160 cm^{-1}. Taking into account the possible[15] existence of the hypothetical AuF_7 molecule, one can suggest that the valence shell of AuF_6^- has enough room to accomodate the seventh electron pair, which, unlike the other electron pairs, is stereochemically active. Therefore, the structure of the AuF_6^- anion would presumably be distorted upon the structural transition of the regular octahedron into a one-cap octahedron (1—3—3 coordination), in which the bonding and nonbonding electron pairs interact only slightly.[16]

Compounds $ClX_2^+AuF_6^-$ (X = F, O). The vibrational spectra of more than ten salts of ClF_3 and ClO_2F with Lewis acids of moderate strengths (BF_3, AsF_5, SbF_5) have been studied by now.[17—19] The assignment of frequencies in the spectra of the $ClX_2^+MF_6^-$ salts (M = As, Sb) is difficult due to the substantial interactions between the cation and the anion.[19] Study of the crystal structure of $ClF_2^+MF_6^-$ (M = Nb, Ta) has shown[20] that the cation—anion interaction noticeably influences the lengths of some M—F bonds in the octahedral anions.

The ClX_2^+ cation, unlike linear triatomic molecules ($D_{\infty h}$ symmetry), is a bent structure corresponding to a C_{2v} point group of symmetry (the (Cl—F) and (Cl—O) bond lengths are 1.65 and 1.47 Å, respectively, and the X—Cl—X angles are 99.1±1.4° and 106.5±1.8° for X = F and O, respectively[21]) and having three normal modes with the following types of symmetry:

$$\Gamma_{vib} = 2A_1\ (\text{IR, Raman}) + B_1\ (\text{IR, Raman}),$$

which are active both in the IR and Raman spectrum.

The relationship between the frequencies of the antisymmetrical and symmetrical stretching modes[10] in the vibrational spectra of compounds $ClX_2^+AuF_6^-$, both solid and as solutions in HF (Tables 1, 2), corresponds to that observed for most linear and bent molecules of the XY_2 type, namely, $\nu_3 > \nu_1$. The lines for all three vibrations of the ClX_2^+ cation in the spectra of solid compounds are split into two components. According to the published data,[10] this splitting is due to the fact that the vibrational spectra of ClX_2^+ exhibit Cl—O and Cl—F vibrations of two isotope modifications, $^{35}ClX_2^+$ and $^{37}ClX_2^+$; as a rule, this is indicated by two facts: the lines corresponding to vibrations of the ^{37}Cl—X bond occur at lower frequencies and are approximately 3—4 times less intense than the corresponding lines due to the ^{35}Cl—X bond. However, these criteria are observed only for the ClO_2^+ cation. In the case of the ClF_2^+ cation, conversely, the line of the antisymmetrical $\nu_3(B_1)$ mode in both spectra of $^{37}ClF_2^+$ and the line of the deformation $\nu_2(A_1)$ mode in its Raman spectrum are substantially stronger than the corresponding lines for $^{35}ClF_2^+$. This situation largely resembles that observed in molecular crystals upon the known Davydov splitting,[22] which occurs when a crystal unit cell contains several chemically identical molecules arranged at an angle to one another and having, correspondingly, several levels of excited states. All of the splitting components are not necessarily displayed in the IR and Raman spectra, because they obey the selection rules with respect to the group-factor symmetry. Since the Davydov splitting is proportional to the strength of the transition oscillator,[22] the greatest splitting is observed for those lines in the Raman spectra whose frequencies are close to the frequencies of IR-active vibrations having relatively large oscillator strengths. The magnitude of the Davydov splitting is normally less than 3 cm^{-1}, although sometimes it reaches 10—15 cm^{-1}. Thus, although the vibrational spectra of ClO_2^+ and ClF_2^+ in $ClX_2^+AuF_6^-$ are similar, it can be assumed that the origin of band splitting for these cations is different. In addition, whereas the nature of the doublets in the spectra of ClO_2^+ is almost beyond doubt, in the case of ClF_2^+, the suggestion concerning the Davydov splitting requires experimental verification (by polarization spectroscopy of $ClF_2^+AuF_6$ single crystals), which is difficult to perform in practice.

In the Raman spectra of both compounds in the solid state, the $\nu_1(A_{1g})$ line of the AuF_6^- anion is split into two components. Apparently, this is due to the insignificant tetragonal distortions of the octahedral structure[23] of AuF_6^- in the crystal lattice field, which can lead to a lower symmetry of the anion *via* a sequence of structural transformations of the $O_h \rightarrow D_{4h}$, $O_h \rightarrow C_{4v}$, *etc.* type, observed for some other hexafluoro complexes.[16] This assumption is supported by the fact that the line of the ν_3 mode, forbidden by the selection rules, appears in the Raman spectrum at ~640 cm^{-1}. In addition, the splitting of the ν_1 line in the Raman spectra of the AuF_6^- anion may also be due to the intrinsic asymmetry of the $ClX_2^+AuF_6^-$ complex resulting from the perturbing influence of lower-symmetry excited electron states on the O_h symmetry of the ground state. It is hardly possible to separate the effects of intrinsic asymmetry and the crystal lattice based on the data of vibrational spectra.[23] Yet another possible reason for this splitting in the spectrum of $ClF_2^+AuF_6^-$ is the decrease in the symmetry of the anion due to the tendency to form stable F-bridges between anions and cations, which is clearly pronounced in the salts of the $ClF_2^+X^-$ type.[16] Meanwhile, the structure of AuF_6^- in an HF solution strictly corresponds to the O_h point group.

Table 1. Experimental frequencies (ν) in the vibrational spectra of $ClF_2^+AuF_6^-$ and their assignment

ν/cm^{-1}			Assignment and types of vibrations	
Raman		IR,		
solid phase	a solution in HF	solid phase	AuF_6^- (O_h)	ClF_2^+ (C_{2v})
224 (29)	228 (21)	—		
230 sh		—	$\nu_5(F_{2g})$, δ_s(F—Au—F)	
385 (7)	379 (5)	377 sh		
392 sh	—	382 m		$\nu_2(A_1)$, δ(F—Cl—F)
531 (5)	528 (3)	—	$\nu_2(E_g)$, ν_s(Au—F)	
583 (77)		—		
594 (100)	590 (100)	—	$\nu_1(A_{1g})$, ν_s(Au—F)	
641 (3)	—	637 v.s	$\nu_3(F_{1u})$, ν_{as}(Au—F)	
791 (3)	789 (10)	790 sh		
797 (14)	—	795 s		$\nu_1(A_1)$, ν_s(Cl—F)
802 (4)	800 sh	803 m		
812 (1)	—	816 m		$\nu_3(B_1)$, ν_{as}(Cl—F)
—	—	1159 v.w		$\nu_1+\nu_2$ (A_1)
—	—	1573 w		$\nu_1+\nu_3$ (B_1)

Note. Designations: ν is stretching, δ is deformation, s is symmetrical, and as is antisymmetrical vibration, vs is very strong, s is strong, m is medium, w is weak, and vw is a very weak band. For Raman frequencies, the intensities of the corresponding lines are given in conventional units.

Table 2. Experimental frequencies (ν) in the vibrational spectra of $ClO_2^+AuF_6^-$ and their assignment

ν/cm^{-1}			Assignment and types of vibrations	
Raman		IR,		
solid phase	a solution in HF	solid phase	AuF_6^- (O_h)	ClO_2^+ (C_{2v})
224 (37)	228 (24)	—		
233 sh		—	$\nu_5(F_{2g})$	
512 sh	—	514 sh		
519 (4)	522 (2)	518 s		$\nu_2(A_1)$, δ(O—Cl—O)
589 (87)		—		
595 (100)	598 (100)	—	$\nu_1(A_{1g})$	
642 (3)	—	635 v.s	$\nu_3(F_{1u})$	
1043 (3)	—	1045 sh		
1055 (11)	1051 (7)	1058 w		$\nu_1(A_1)$, ν_s(Cl—F)
1280 (≤2)		1283 w		
1296 (4)	1290 (4)	1297 m		$\nu_3(B_1)$, ν_{as}(Cl—F)

Note. The designations are explained in Table 1.

Compound $ClOF_2^+AuF_6^-$. Chlorine oxytrifluoride, like chloryl fluoride, exhibits amphoteric properties; this is due to the strained structure of its molecule,[18,19] which distinguishes it from highly symmetrical perchloryl fluoride. The complex compounds of $ClOF_3$ with five-coordinate Lewis acids of the YF_5 type (Y = As, Sb, P, *etc.*) have been studied fairly comprehensively[18] by vibrational and ^{19}F NMR spectroscopy.

The $ClOF_2^+$ cation can exist with equal probability in two configurations, pyramidal (C_s symmetry) and planar (C_{2v} symmetry)[24]; these configurations are virtually indistinguishable in the vibrational spectra. All six vibrations characterizing the two structures and having the types of symmetry

$$\Gamma_{vib} = 4A' \text{ (IR, Raman)} + 2A'' \text{ (IR, Raman)} \quad (C_s)$$

and
$$\Gamma_{vib} = 3A_1 \text{ (IR, Raman)} + B_1 \text{ (IR, Raman)} + 2B_2 \text{ (IR, Raman)} \quad (C_{2v})$$

are active both in the IR and Raman spectra. The only way to distinguish these structures is to perform polarization measurements in the Raman spectra; the pyramidal structure of $ClOF_2^+$ (C_s) accounts for four polarized lines, whereas the planar cation (C_{2v}) is responsible for three lines. The set of spectroscopic, quantum-chemical, and dynamic data[24] led to the conclusion that complexation of $ClOF_3$ with Lewis acids of the AF_n type (A = H, B, Au; n = 1, 3, 5, respectively) can occur *via* two channels, either through axial F ligands in the case of moderate-strength acids such as HF or BF_3 to give the pyramidal C_s configuration or through an equatorial F ligand in the case of the abnormally strong Lewis acid, AuF_5. When the process occurs *via* the second channel, the strong field of the AuF_6^- anion in combination with the solvent field induces structural nonrigidity of the $ClOF_2^+$ cation and transforms it into the unique T-shaped planar configuration, known[18] only for ClF_3 and BrF_3. Geometric parameters for the T-shaped planar $ClOF_2^+$ cation have been calculated.[24]

The line frequencies in the vibrational spectra of $ClOF_2^+AuF_6^-$ in the solid phase and in solution in anhydrous HF are presented in Table 3. The assignment of the spectral frequencies of the $ClOF_2^+$ cation, unlike that reported previously,[17] was carried out assuming the T-shaped planar configuration of $ClOF_2^+$. The $\nu_1(A')$ line of the $ClOF_2^+$ cation in the vibrational spectra of

Table 3. Experimental frequencies (ν) in the vibrational spectra of $ClOF_2^+AuF_6^-$ and their assignment

ν/cm^{-1}			Assignment and types of vibrations	
Raman		IR,		
solid phase	a solution in HF	solid phase	AuF_6^- (O_h)	$ClOF_2^+$ (C_{2v})
222 (37)				
230 sh	218 (16)	—	ν_5 (F_{2g})	
387 (4)	385 (2)	381 sh		ν_4(A′), δ_s(F—Cl—O)
405 (4)	402 (2)	404 w		ν_6(A″), δ_{as}(F—Cl—O)
505 (1)	502 (≤1)	510 m		ν_3(A′), δ_s(Cl—F)
519 (3)	513 (2)	—	$\nu_2(E_g)$	
594 sh		—		
599 (100)	597 (100)	—	$\nu_1(A_{1g})$	
657 (2)	649 sh	647 v.s	$\nu_3(F_{1u})$	
698 sh	714 sh	705 s		ν_5(A″), ν_{as}(Cl—F)
741 (10)	747 (7)	733 m		ν_2(A′), ν_s(Cl—F)
1328 (3)	1327 (2)	1319 w		
1341 sh	1338 sh	1330 m		ν_1(A′), ν_s(Cl—O)

Note. The designations are explained in Table 1.

crystalline $ClOF_2^+AuF_6^-$ and its solution in HF is split into two components. A similar splitting of the ν_1 line was observed in the vibrational spectrum[25] of an isoelectronic compound, SOF_2; it is associated with the Fermi resonance between the ν_1(A′) and $\nu_2+\nu_3$(A′) states (ν_1 = 1329, 1339 cm^{-1}; ν_2 = 808 cm^{-1}; ν_3 = 530 cm^{-1}). The frequency of the $\nu_2+\nu_3$ compound vibration of the $ClOF_2^+$ cation, unlike that for SOF_2, is shifted to the long-wave region of the spectrum with respect to the ν_1(A′) frequency by approximately 80 cm^{-1} and amounts to ~1250 cm^{-1}; therefore, the contribution of the Fermi resonance to the splitting of the ν_1 line of the $ClOF_2^+$ cation should be relatively small. As in the case of the ClF_2^+ cation, these features of the spectra of $ClOF_2^+AuF_6^-$ might be due to Davydov splitting.

As in the vibrational spectra of $ClX_2^+AuF_6^-$ (see Tables 1, 2), the splitting of the $\nu_1(A_{1g})$ line of the AuF_6^- anion, observed in the Raman spectra of crystalline $ClOF_2^+AuF_6^-$, and the fact that the line for the $\nu_3(F_{1u})$ mode, forbidden by the selection rules, occurs in this spectrum at ~650 cm^{-1} may be due to tetragonal distortions of the octahedral structure of the hexafluoroaurate ion in the crystal lattice field, the formation of F bridges between the cation and the anion, and the intrinsic asymmetry of AuF_6^-.

Compound $ClF_4^+AuF_6^-$. The electron-donating capacity of chlorine pentafluoride, having a tetragonal-bipyramidal structure (C_{4v}), is somewhat lower than that of chlorine trifluoride; in addition, ClF_5, unlike ClF_3, does not possess electron-withdrawing capacity.[18,26] Complex compounds formed by ClF_5 with Lewis acids like YF_5 (Y = As, Sb, *etc.*) have been studied[18,27] by vibrational and ^{19}F NMR spectroscopy. The transformation of ClF_5 into ClF_4^+, which has two two-center bonds and one three-center four-electron bond, is accompanied by an almost twofold increase in the force constant of the equatorial bond, whereas the change in the force constant of the axial bond[27] is slight. This indicates that bonding in the equatorial plane may occur *via* sp^2 hybridization, whereas the axial bonding may be due to the involvement of one p-electron pair of the Cl atom in the formation of a semiionic three-center four-electron ppσ bond.

The ClF_4^+ cation has the structure of a trigonal bipyramid (TBP) (a distorted tetrahedron with C_{2v} symmetry: the Cl—F_{eq} and Cl—F_{ax} bond lengths are 1.57 and 1.66 Å, respectively; the F_{eq}—Cl—F_{eq}, F_{eq}—Cl—F_{ax}, and F_{ax}—Cl—F_{ax} bond angles are 97°, 90°, and 180°, respectively) in which the lone electron pair occupies an equatorial position.[27] This bisphenoid is characterized by nine normal modes corresponding to the following types of symmetry:

$$\Gamma_{vib} = 4A_1 \text{ (IR, Raman)} + A_2 \text{ (Raman)} + 2B_1 \text{ (IR, Raman)} + 2B_2 \text{ (IR, Raman)}.$$

All these vibrations are active in the Raman spectrum and eight of them (A_1, B_1, and B_2) are IR-active. When analyzing the spectrum of the ClF_4^+ cation, whose main configuration is a TBP, one should bear in mind that intramolecular ligand exchange[15,28] can occur in this structure according to several mechanisms without substantial energy costs. The simplest mechanism is inversion *via* a square planar D_{4h} configuration. Since only one minimum-energy pathway (MEP) leads from each bisphenoid configuration to the planar configuration, whereas transition from the planar to bisphenoid configuration can occur *via* four pathways, the potential surfaces (PS) for the inversion can be divided into quadruples of bisphenoid structures, which pass into one another *via* the common D_{4h} configuration. The intramolecular ligand exchange in ClF_4^+ also can occur *via* two schemes similar to the Berry pseudo-rotation mechanism.[29] In one case, the top of the barrier on the PS is matched by a square-pyramidal configuration with C_{4v} symmetry, and in the other case, by a TBP with C_{3v} symmetry. There are eight independent TBP configurations (C_{3v}) and each C_{2v} configuration has two MEP leading to TBP.

Our estimates carried out resorting to the published data[28] showed that the smallest activation energy characterizes the $C_{2v} \rightleftharpoons C_{4v}$ rearrangement (Berry pseudorotation, H_{pr} = 2.0 kcal mol^{-1}); for the $C_{2v} \rightleftharpoons C_{3v}$ transition, this value is an order of magnitude larger (H_{pr} = 22.5 kcal mol^{-1}). As regards the inversion *via* a planar square pyramid $C_{2v} \rightleftharpoons D_{4h}$, the height of its barrier (H_{inv} = 178 kcal mol^{-1})[28] for an isolated ClF_4^+ cation is of the same order of magnitude as this value in the case of an isoelectronic compound, SF_4 (H_{inv} = 118 kcal mol^{-1}).[15] A lower barrier to the $C_{2v} \rightleftharpoons C_{3v}$ rearrangement may be obtained by using more complete basis sets and by taking into account the correlation energy.[24] However, our analysis[26] of the role of the polarization d-functions of the central atom and the electron correlation effects indicates that the results obtained are consistent with the small pseudo-rotation mechanism, resulting in a square-pyramidal configuration. The square pyramid (C_{4v}), like TBP (C_{2v}), is characterized by nine normal modes corresponding to the symmetry types

$$\Gamma_{vib} = 3A_1 \text{ (IR, Raman)} + 2B_1 \text{ (Raman)} + \\ + B_2 \text{ (Raman)} + 3E \text{ (IR, Raman)};$$

six modes, ν_1, ν_2, ν_3 (A_1) and ν_7, ν_8, ν_9 (E), are active in the IR spectrum, and all nine modes are Raman-active.

The maxima of the vibration bands in the vibrational spectra of $ClF_4{}^+AuF_6{}^-$ in the solid phase and in the HF solution are presented in Table 4. The observed frequencies were assigned by analogy with those[27] for the complex compounds of ClF_5 with acids YF_5 (Y = As, Sb), assuming that $ClF_4{}^+$ occurs in a TBP configuration. Analysis of the data presented in Table 4 reveals some abnormal features in the vibrational spectrum of $ClF_4{}^+AuF_6{}^-$. The IR and Raman spectra of the $ClF_4{}^+$ cation in the solid phase and in solution in HF contain seven lines instead of nine lines, which should be observed in the case of both a TBP and a square pyramid with C_{2v} symmetry. The assignment of the intense line at ~580 cm^{-1} (Raman) and 571 cm^{-1} (IR) to the $\nu_2(A_1)$ mode seems doubtful because the ν_2 band in the IR spectrum of $ClF_4{}^+YF_6{}^-$ (Y = As, Sb) is weak.[27] Meanwhile, the intensity of this line in the Raman spectrum is more than 4 times greater than that of the line with a frequency of ~800 cm^{-1}, which was assigned, resorting to the published data,[27] to the fully symmetrical $\nu_1(A_1)$ mode of the $ClF_4{}^+$ cation and which is the most intense line in the Raman spectra of $ClF_4{}^+YF_6{}^-$ (Y = As, Sb). The assignment of the line at ~580 cm^{-1} (Raman) to the fully symmetrical $\nu_1(A_1)$ mode of the $AuF_6{}^-$ anion is not quite correct because distortion of the octahedral structures of hexafluoro-anions is normally accompanied by the appearance of a ν_3 line, forbidden[10] in the Raman spectrum. Even if one assumes that the distortion of the $AuF_6{}^-$ structure results in the ν_1 line being manifested in the IR spectrum, its intensity, comparable with the intensity of the band corresponding to the antisymmetrical stretching vibration of $AuF_6{}^-$, is too high. Thus, the abnormal features found in the vibrational spectrum of the $ClF_4{}^+$ cation occurring in the strong $AuF_6{}^-$ field, which is able to induce[24] the energetically less favorable $C_{2v} \rightleftharpoons C_{3v}$ rearrangement, do not answer the question of what is the structure of the $ClF_4{}^+$ cation in the compound being considered. As regards the $AuF_6{}^-$ anion, the appearance of the low-intensity line due to the antisymmetrical vibrations at 635 cm^{-1} in the Raman spectrum and the possible splitting of the $\nu_1(A_1)$ line is due to reasons similar to those described above.

Table 4. Experimental frequencies (ν) in the vibrational spectra of $ClF_4{}^+AuF_6{}^-$ and their assignment

ν/cm^{-1}			Assignment and types of vibrations	
Raman		IR,		
solid phase	a solution in HF	solid phase	$AuF_6{}^-$ (O_h)	$ClF_4{}^+$ (C_{2v})
227 (37)	221 (18)	—	$\nu_5(F_{2g})$	
239 sh	—			
376 (4)	—	381 m		$\nu_9(B_2)$, $\delta_{op}(F_{ax}—Cl—F_{ax})$
512 (1)	515 (≤1)	510 w		$\nu_3(A_1)$, $\delta_s(F_{eq}—Cl—F_{ax})$
531 (2)	535 (≤1)	—	$\nu_2(E_g)$	
546 sh	551 (≤1)	542 w		$\nu_7(B_1)$, $r(F_{eq}—Cl—F_{eq})$
581 (93)	577 (80)	571 s	$\nu_1(A_{1g})$ or $\nu_2(A_1)$,	$\nu_s(Cl—F_{ax})$
600 (100)	598 (100)	—	$\nu_1(A_{1g})$	
635 (5)	—	642 v.s	$\nu_3(F_{1u})$	
786 sh	779 sh	776 sh		$\nu_6(B_1)$, $\nu_{as}(Cl—F_{ax})$
796 (21)	788 (19)	795 s		$\nu_1(A_1)$, $\nu_s(Cl—F_{eq})$
812 sh	806 sh	816 sh		$\nu_8(B_2)$, $\nu_{as}(Cl—F_{eq})$
—	—	1327 w		$\nu_2+\nu_4(B_1)$

Note. r is a rocking vibration; δ_{op} is an out-of-plane deformation vibration; the other designations are explained in Table 1.

Compound $ClF_6{}^+AuF_6{}^-$. Three salts containing the $ClF_6{}^+$ cation are known: $ClF_6{}^+XF_6{}^-$ (X = As, Sb, Pt)[18,30]; the vibrational and the ^{19}F NMR spectra of these salts have been studied. The absence[19] of fast relaxation due to interaction of the quadrupole Cl nucleus with a nonsymmetrical electric field gradient induced by the F ligands in the NMR spectra attests to a highly symmetrical structure of $ClF_6{}^+$.

The $ClF_6{}^+$ cation is octahedral[18,19,30] and, like $AuF_6{}^-$, it is characterized by six normal modes. The vibration band maxima in the spectra of $ClF_6{}^+AuF_6{}^-$ in the solid state and in solution in HF recorded in our work are presented in Table 5. In conformity with the strict selection rules, the Raman spectrum of the $ClF_6{}^+$ cation exhibits three lines with frequencies 686, 624, and 515 cm^{-1} (see Table 5), which were assigned to the ν_1, ν_2, and ν_5 modes of the octahedral structure, respectively. The IR spectrum of $ClF_6{}^+$ exhibits two absorption bands with maxima at 691 and 587 cm^{-1}, which were assigned to the ν_3 and ν_4 modes, respectively. A distinctive feature of the Raman spectrum of the $ClF_6{}^+$ cation in the solid phase is the presence of a low-intensity line with a maximum at 705 cm^{-1}. This band appears apparently due to the Fermi resonance of the $\nu_1(A_{1g})$ and $2\nu_6(A_{1g}+E_g+F_{1g}+F_{2g})$ states, and, therefore, we assigned it to the first overtone of the $\nu_6(F_{2u})$ mode inactive in both types of spectra. This allowed us to determine the frequency of this vibration (ν_6 ~352 cm^{-1}), which differs insignificantly from that for SF_6 (ν_6 ~347 cm^{-1}).[10,13] Theoretical estimates[14] of the ν_6 vibration frequency for

Table 5. Experimental frequencies (ν) in the vibrational spectra of $ClF_6^+AuF_6^-$ and their assignment

ν/cm^{-1}			Assignment and types of vibrations	
Raman		IR,		
solid phase	a solution in HF	solid phase	AuF_6^- (O_h)	ClF_6^+ (O_h)
226 (33)	221 (24)	—		
231 sh	—	—	$\nu_5(F_{2g})$	
515 (4)	512 sh	—		$\nu_5(F_{2g})$, δ_s(F—Cl—F)
527 (6)	522 (2)	—	$\nu_2(E_g)$	
—	—	587 w		$\nu_4(F_{1u})$, δ_{as}(F—Cl—F)
591 (85)	—	—		
598 (100)	589 (100)	—	$\nu_1(A_{1g})$	
624 (2)	618 (≤1)	—		$\nu_2(E_g)$, ν_s(Cl—F)
—	—	653 s	$\nu_3(F_{1u})$	
686 (10)	683 (7)	—		$\nu_1(A_{1g})$, ν_s(Cl—F)
705 (≤1)	—	—		$2\nu_6(A_{1g}+E_g+F_{1g}+F_{2g})$
—	—	891 m		$\nu_3(F_{1u})$, ν_{as}(Cl—F)

Note. The designations are explained in Table 1.

the ClF_6^+ cation gave a value of ~357 cm^{-1}. Thorough analysis of the contour of bands in the IR spectrum revealed the isotopic structure of the ν_3 band, which, in turn, permitted us to measure the isotope shift for this vibration (~13.0 cm^{-1}). The estimates of the isotope shift of $\Delta\nu_3$, carried out using the semiempirical formula for hexafluoride molecules[14]

$$\Delta\nu_3\ (\mathrm{cm^{-1}\ (amu)^{-1}}) = 4.20\nu_3 \cdot m^{-1.75}$$

(ν_3 is the frequency of the fundamental band (cm^{-1}), m is the weight of the central atom (amu)), give ~14 cm^{-1}, which virtually coincides with the experimental ν_3 value.

Unlike the spectra of the compounds considered above, in the Raman spectra of $ClF_6^+AuF_6^-$, only splitting of the $\nu_1(A_{1g})$ line is observed and, in conformity with the selection rules,[10] the line of the IR-active $\nu_3(F_{1u})$ mode is absent. This fact indicates that in the $ClF_6^+AuF_6^-$ salt, the cation—anion interactions are weakened and the distortion of the octahedral structure of the anion may be mostly due to the effect of the crystal lattice field.

Thus, the results obtained here indicate the diversity of spectroscopic manifestations of the structural effects in the complex compounds of AuF_5, associated with some physicochemical features of cations and the anion.

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