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Vibrational spectra of AuF_5 complexes with nitrogen fluorides and oxofluorides

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Vibrational spectra and structural features of AuF_5 complexes with nitrogen fluorides (NF_3, N_2F_4) and oxofluorides (FNO, NF_3O) are investigated. Vibrational frequency assignment in the solid phase and in solution of anhydrous HF was made. Distinctive features of vibrational spectra of $X^+AuF_6^-$ ($X = NF_4^+, N_2F_3^+, NO^+, NOF_2^+$) related to structural transformations of cations and hexafluoroaurate anion due to the influence of the crystal field and cation—anion interactions are discussed.

Key words: nitrogen fluorides and oxofluorides, Lewis acid, cation—anion interactions, hexafluoroaurate anion.

Particular interest in nitrogen fluorides and oxofluorides (NF_3, N_2F_4, N_2F_2, FNO, FNO_2, NF_3O) and their complexes with Lewis acids is due to the fact that these systems are energetic compounds and can be used as strong fluoro oxidants in inorganic synthesis of fluorine-containing compounds and for solving various applied problems.[1—3] Such compounds are used in nanotechnologies when conducting controlled reactions (including cryoreactions) of atoms, molecules, clusters, and nanoparticles on various surfaces,[4] in technologies for nuclear fuel processing,[5] and chemistry of molten salts.[6] They can also be used for the synthesis of homoleptic polynitrogen compounds whose existence was predicted in many quantum chemical studies.[7] According to various estimates, the properties and performance of polynitrogen compounds as monopropellants can improve the corresponding properties of hydrazine and appear to be superior to those of composite propellants.[8]

Polynitrogen compounds may seem to be promising explosives because extraordinary ability of these environmentally safe molecules to release large amounts of energy compared to the most powerful energetic materials, namely, hexanitrohexaazaisowurtzitane (CL-20) and octanitrocubane (ONC), gave an impetus to research on the determination of the possibility for other promising polynitrogen compounds to exist.[9]

Recently, important key blocks were established for the complexes with N_k^+ ($k \geq 5$) and N_7O^+ cations produced in the reactions of nitrogen fluorides and oxofluorides with Lewis acids (BF_3, SbF_5, PF_5, *etc.*).[10,11] The use of NF_4^+, $N_2F_3^+$, N_2F^+, and NOF_2^+ cations as components of the complexes with AuF_5 (abnormally strong Lewis acid) in such blocks can make feasible the synthesis of novel energetic materials based on polynitrogen compounds.

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Earlier,[12] we have studied the IR and Raman spectra of AuF_5 complexes with chlorine fluorides and oxofluorides. It was shown that vibrational spectroscopy, which combines high sensitivity and the possibility of detailed investigations of various spectroscopic effects,[13] makes it possible to obtain reliable information on the structural features and on the nature of chemical bonds in gold pentafluoride complexes which are highly reactive similarly to AuF_5.[14]

In this work, we report the results of our studies of the vibrational spectra and structural features of $NF_4^+AuF_6^-$, $N_2F_3^+AuF_6^-$, $NO^+AuF_6^-$ and $NOF_2^+AuF_6^-$ complexes in which NF_4^+, $N_2F_3^+$, NO^+, and NOF_2^+ cations are stabilized by AuF_6^- octahedral anion.

Experimental

Hexafluoroaurates NF_4AuF_6, $NOAuF_6$, $N_2F_3AuF_6$, and NOF_2AuF_6 were synthesized in solutions in anhydrous hydrogen fluoride by fluorination of metallic gold (foil with Au content > 99.99 mass %) with krypton difluoride (purity >99.5 mass %) at $T < 293$ K in the presence of corresponding gaseous reactant following a known procedure.[15] Owing to high solubility of AuF_5, complexation in HF solutions proceeds rapidly and quantitatively and transformation of gold in the presence of NF_3, NOF, N_2F_4, and NOF_3 gives corresponding stable salts.

All operations related to the synthesis of the starting reactants and products were carried out on a tailor-made vacuum bench with metallic supply lines and bleed traps cooled with liquid nitrogen. Complexes were synthesized in minireactors made of transparent fluoroplastic 4-MB.

Commercially available nitrogen trifluoride (TU 6-02-2-852-85, purity 99.2 vol.%) was used. Tetrafluorohydrazine was obtained by the reaction of NF_3 with copper flakes in a flow reactor made of stainless steel, and nitrosyl fluoride was prepared by the reaction of anhydrous $NOBF_4$ and NaF ("chemically pure" grade) in a nickel flow reactor at 450 K.[16] Nitrogen oxotrifluoride was synthesized following a procedure for the synthesis of KrF_2 by the action of fluorine atom beams on nitrosyl fluoride in a cylindrical aluminum thermocatalytic reactor at 77 K (see below).

Thermally and thermodynamically unstable krypton difluoride was synthesized under conditions of thermocatalytic dissociation of molecular fluorine and subsequent reaction of fluorine atoms with solid krypton on the reactor wall cooled with liquid nitrogen (77 K) to stabilize the compound. Spatial separation of the zones of the generation of fluorine atoms and the synthesis of krypton difluoride was ensured by creating a high temperature gradient (500—1000 K cm^{-1}) between the zones and using a catalyst for heterogeneous reaction of molecular fluorine dissociation. Fluorine atoms were generated by the surface of nickel catalyst (nickel coil) heated to 900—1000 K and positioned coaxially with the aluminum cylindrical reactor. Catalytic dissociation of molecular fluorine and generation of fluorine atoms have been studied in detail earlier.[17,18]

Gaseous krypton was preliminarily condensed on the reactor wall at 77 K. Then, molecular fluorine (30—40 Torr) was supplied to the reactor in the presence of catalyst heated to 1000 K at a rate equal to the consumption rate of F_2 in order to maintain the fluorine pressure at a constant level during the synthesis. After completion of the reaction recognized by ceasing fluorine consumption, the reactor was slowly defrosted, the unreacted krypton was condensed into a collector, and the reactor temperature was raised to ambient temperature. Crypton difluoride was condensed into a collector cooled with liquid nitrogen or solid carbon dioxide.

IR absorption spectra of solid samples (finely disperse powders placed in a hermetically sealed Teflon protecting casing between AgCl plates) were studied with a Perkin—Elmer-325 spectrophotometer in the 400—3000 cm^{-1} range. The spectral slit width was 2.5—3.0 cm^{-1}.

Raman spectra were recorded with a Dilor RTI-30 Raman spectrometer using a conventional 90° illumination geometry. The spectral slit width was maintained constant at 3.7 and 2.0 cm^{-1} for solid samples and their solutions in anhydrous HF, respectively. The excitation sources were a 500-mW LGN-503 Ar^+ laser (excitation line at $\lambda = 488$ nm) and a 50-mW LGN-104 He—Ne laser (excitation line at $\lambda = 632.8$ nm). In carrying out polarization measurements, a polaroid analyzer was mounted between the condenser ($F = 50$ mm, $d : r = 1 : 1.8$) and the input slit of the spectrometer. The direction of polarization of excitation laser light was changed by the polarizer (a $\lambda/2$ plate). This procedure for observation of the Raman spectra made it possible to exclude the instrumental polarization correction.[19] The Raman spectrometer was calibrated in λ units using the spectral lines of electric discharge in a Ne lamp ($\lambda = 493$—520 nm) and some lines in the Raman spectrum of liquid indene.

As in the case of AuF_5 complexes with chlorine fluorides and oxofluorides,[12] the samples under study were placed in transparent fluoroplastic 4-MB tubes, the temperature of the samples was maintained at 292±2 K with a water thermostat. The concentrations of AuF_5 complexes in HF were determined to an accuracy of 5—10%. Hydrogen fluoride was thoroughly dried. All operations related to the synthesis of samples were carried out in a box in dry argon atmosphere.

The spectra were processed using appropriate software. The accuracy of determination of spectral line maxima in the IR and Raman spectra was ≤1.5 and 1.0 cm^{-1}, respectively.

Results and Discussion

To date, the physicochemical properties, as well as vibrational, microwave, and NMR spectra, structural features, and the character of bonds in almost all known nitrogen fluorides and oxofluorides have been studied.[1,2,11,20] A feature of some molecules consists in the existence of isomers that have the same symmetry, being structurally different.

This, in particular, concerns FNO molecules that can exist in two isomeric forms, F—N=O and F—O=N, both having a C_s symmetry and different structures. According to microwave spectroscopy data,[21] the geometric parameters of F—O=N are as follows: R(O—N) = 1.336±0.003 Å, R(N—F) = 1.512±0.005 Å, the F—O—N angle is 119.9°, whereas for F—N=O one has R(O—N) = 1.27 Å, R(N—F) = 1.55 Å, and the F—N—O angle is 113.0°.[22]

Molecules N_2F_2 also exist as two isomers, *cis*-N_2F_2 (C_{2v} symmetry) and *trans*-N_2F_2 (C_{2h} symmetry), their ratio in the mixture being 9 : 1.[23]

Depending on the angle of internal rotation, N_2F_4 molecules can exist as three isomers, *viz.*, *trans*-N_2F_4 (C_{2h} symmetry), *gauche*-N_2F_4 (C_2 symmetry), and *cis*-N_2F_4 (C_{2v} symmetry).[24] Deviation of the N—NF_2 fragment from planarity is due to the presence of the lone electron pair at nitrogen atom. Therefore, N_2F_4 exists as a *trans*- or *gauche*-isomer, or as their mixture.[24]

The N—F, N—N, and N—O bond lengths, as well as the corresponding bond angles and vibrational frequencies of nitrogen fluorides and oxofluorides determined by microwave spectroscopy and gas-phase electron diffraction are summarized in Table 1. For some molecules, shown are the results of quantum chemical calculations. Also, for all values from Table 1 listed are methods of investigation and corresponding references. As can be seen, the N—O bond length in the FNO and NF_3O molecules varies insignificantly, whereas the N—F bond lengths change considerably on going from nitrogen fluorides to oxofluorides.

As mentioned earlier,[12] AuF_5 complexes were studied by Raman spectroscopy. Wide use of this method is due to the fact that for high symmetry of the structures of the compounds under study (O_h, T_d, *etc.*), the number of the Raman active vibrations is 1.5—2 times larger than that of the IR active vibrations.[42] The Raman spectra of some AuF_5 complexes with nitrogen fluorides and oxofluorides are shown in Fig. 1.

Compound $NF_4{}^+AuF_6{}^-$. The synthesis and some physicochemical properties of complex salts containing $NF_4{}^+$ cation were for the first time reported in 1967.[43] At present, there is a large number of complexes comprising $NF_4{}^+$ cation and $XF_4{}^-$ (X = B, Al, Br), $YF_5{}^-$ (Y = Ge, Ti, Sn) and $ZF_6{}^-$ (Z = P, As, Sb, Bi, Cr, Pt) anions (see Refs 44—47 and references cited therein). The vibrational and ^{19}F NMR spectra,[45—49] as well as the stability conditions and the mechanisms of formation and decomposition of some salts containing $NF_4{}^+$ cation were determined.[50]

According to spectroscopic data,[44,46—49] the $NF_4{}^+$ cation has a tetrahedral structure with T_d symmetry. Transformation of NF_3 molecule to $NF_4{}^+$ cation is accompanied by an increase in the force constant of the N—F bond in $NF_4{}^+$, and by strengthening of the N—F bond (f_r = 4.3 mdyn Å^{-1} and R(N—F) = 1.365 Å for NF_3 *vs.* f_r = 6.15 mdyn Å^{-1} and R(N—F) = 1.310 Å^{-1} for $NF_4{}^+$).[48]

The $NF_4{}^+$ cation with T_d symmetry is characterized by four normal vibrations with the symmetry types Γ_{vib} = = A_1 (Raman) + E (Raman) + 2 F_2 (IR, Raman). All four vibrations are Raman active, whereas only two triply de-

Table 1. N—X bond lengths (R), X—N—F (X = O, N, F) bond angles, and corresponding frequencies (ν) of N—X vibrations in molecules comprised of N, F, and O atoms

Molecule	X—N—F		N—F		N—O (N—N)	
	X	Angle/deg	R/Å	ν/cm^{-1}	R/Å	ν/cm^{-1}
NOF	O	110.08±0.15 (MWS)[21]	1.512±0.005 (MWS)[21]	765.8	1.136±0.003 (MWS)[21]	1843.5
		112.5 (C)[26]	1.516 (C)[26]	(see Ref. 25)	1.13155(23) (MWS)[27]	(see Ref. 25)
NOF_3	O	117.1 (GED)[28]	1.434 (GED)[28]	836	1.159 (GED)[28]	1691
	F	100.8 (GED)[28]	1.445 (C)[31]	(see Refs 29, 30)	1.154 (C)[31]	(see Refs 29, 30)
	O	117.38 (C)[31]				
NF_3	F	102.37±0.3 (MWS)[32]	1.365±0.002 (MWS)[32]	1032.0		
		101.84 (MWS)[33]	1.3676 (MWS)[33]	(see Ref. 33)		
cis-N_2F_2	N	114.44±1.0 (GED)[34]	1.410±0.008 (GED)[34]	896	(1.214±0.012) (GED)[34]	(1525)
				(see Refs 35, 36)		(see Refs 35, 36)
				952		
				(see Ref. 35)		
trans-N_2F_2	N	105.50±0.7 (GED)[34]	1.396±0.008 (GED)[34]	1010	(1.232±0.01) (GED)[34]	(1522)
				(see Refs 36, 37)		(see Refs 36, 37)
				990		
				(see Refs 36, 37)		
gauche-N_2F_4	F	105.1±1.0 (GED)[38]	1.375±0.004 (GED)[38]	1009	(1.489±0.007) (GED)[38]	(590)
	N	100.1±1.0 (GED)[38]	1.372±0.002 (GED)[41]	(see Refs 39, 40)	(1.492±0.007) (GED)[41]	(see Refs 39, 40)
	F	103.1±0.6 (GED)[41]				
	N	101.6±0.4 (GED)[41]				
trans-N_2F_4	F	102.9±0.75 (GED)[38]	1.372±0.002 (GED)[41]	1036	(1.492±0.007) (GED)[41]	(600)
	N	100.6±0.6 (GED)[38]		(see Refs 39, 40)		(see Refs 39, 40)
	F	103.1±0.6 (GED)[41]				
	N	101.6±0.4 (GED)[41]				

Note. Notations of methods are as follows: MWS is microwave spectroscopy, GED is gas-phase electron diffraction, and C denotes quantum chemical calculations.

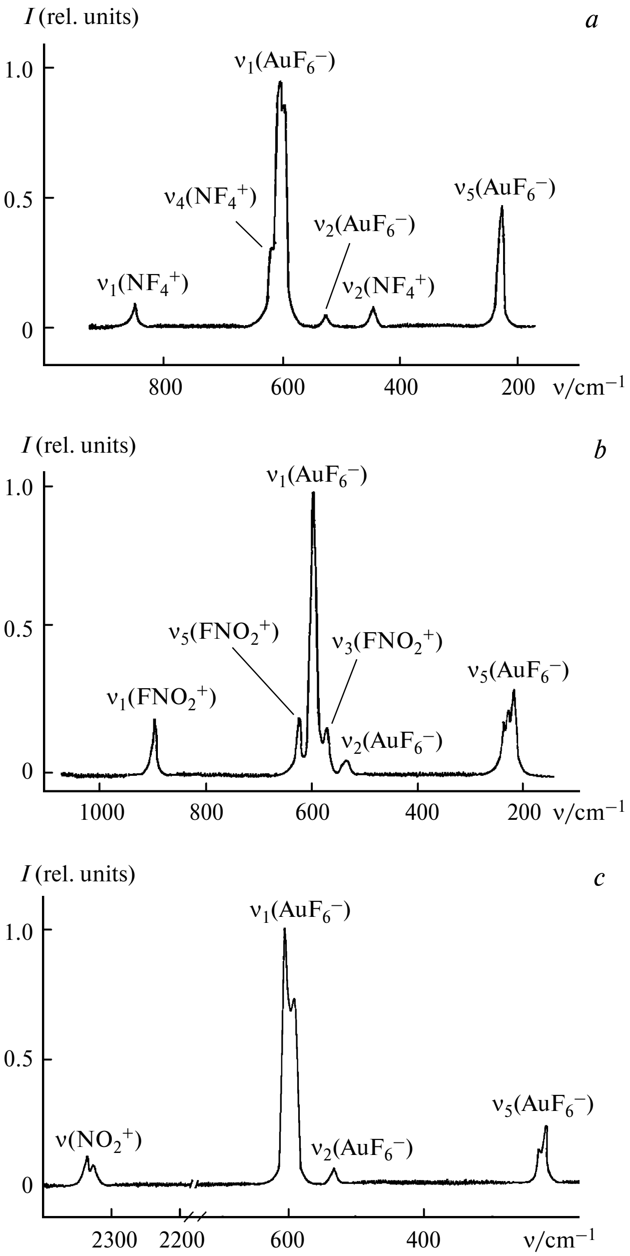


Fig. 1. Raman spectra of crystalline $NF_4^+AuF_6^-$ (*a*), $NOF_2^+AuF_6^-$ (*b*), and $NO^+AuF_6^-$ (*c*).

generate vibrations with the symmetry type F_2 (ν_3, ν_4) are IR active.

The vibrational frequencies of $NF_4^+AuF_6^-$ in the solid state and in solution in HF are listed in Table 2.

Frequency assignment in the spectra of NF_4^+ cation was carried out assuming an undistorted tetrahedral (T_d) structure based on the results of polarization measurements in the Raman spectrum of $NF_4^+AuF_6^-$ solutions in anhydrous HF taking into account the published frequency assignment data.[45,47,49,50] Also, the interpretation of the vibrational spectrum of the isoelectronic analog CF_4 was used.[42]

Frequency assignment for AuF_6^- anion in all complexes of gold pentafluoride with nitrogen fluorides and oxofluorides was made under assumption of undistorted octahedral (O_h) structure based on the results of the assignment[12,15] taking account of polarization measurements in the Raman spectra of their solutions in anhydrous HF.

As can be seen, in accordance with the selection rules for the XY_4 structures with T_d symmetry, the Raman spectrum of NF_4^+ cation exhibits vibrational bands $\nu_1(A_1)$, $\nu_2(E)$, and $\nu_4(F_2)$ at 848, 611, and 442 cm^{-1}, respectively, and its IR spectrum shows a $\nu_4(F_2)$ band and a band of the stretching antisymmetrical vibration $\nu_3(F_2)$ at 1160 cm^{-1}. For both spectra, one has $\nu_3 > \nu_1$ and $\nu_4 > \nu_2$; this is characteristic of almost all tetrahalides with T_d symmetry.[42,51]

The data of Table 2 also indicate a number of anomalies in the spectra of $NF_4^+AuF_6^-$. For instance, the Raman spectrum of NF_4^+ cation shows no line of antisymmetrical stretching vibration, $\nu_3(F_2)$, allowed by the selection rules. *Vice versa*, the IR spectrum of NF_4^+ demonstrates the $\nu_2(E)$ band of symmetrical deformation vibration forbidden by the selection rules. Also, the Raman spectrum of NF_4^+ cation in solid $NF_4^+AuF_6^-$ shows no splitting of the $\nu_3(F_2)$ band of the triply degenerate vibration observed in some studies.[45—49] This splitting is due to positional symmetry[51] and characteristic of XF_4 (T_d) molecules in the solid state. An additional analysis of the Raman spectra of the salt $NF_4^+AuF_6^-$ revealed very weak lines at 490, 502, and 1074 cm^{-1}. Low intensities of these lines are not surprising because, unlike the $NF_4^+XF_6^-$ salts, the intensity ratio of the strongest Raman lines is $\nu_1(NF_4^+) : \nu_1(AuF_6^-) \le 0.15$, whereas the ratios $\nu_1(NF_4^+) : \nu_1(XF_6^-)$ (X = As, Sb, *etc.*)[48,49] lie in the range 0.6—0.8.

These facts suggest noticeable cation—anion interactions in $NF_4^+AuF_6^-$, characteristic of gold pentafluoride complexes.[12] These interactions affect the lengths of some N—F bonds in the tetrahedral cation (according to our estimates, their variation can amount to 0.1 Å). In addition, transformation of NF_3 molecule to NF_4^+ cation can be accompanied by some change in the hybridization of valence orbitals at nitrogen atom and by strengthening of one or two N—F bonds. As a result, the T_d-structure of NF_4^+ cation can be distorted to give C_{3v}- or C_{2v}-structures with nonequivalent fluorine atoms in axial and equatorial positions (Fig. 2).

A possible distortion of the tetrahedral structure of NF_4^+ cation was also suggested in studies[52,53] of the crystal structure and vibrational spectrum of crystalline salt $NF_4^+BF_4^-$. The unit cell of $NF_4^+BF_4^-$ contains two crystallographically independent cations $N(1)F_4^+$ and $N(2)F_4^+$ (space groups 4^- and *mm*, respectively).[52,53] The bond lengths in these cations are noticeably different: $R(N(1)—F(1)) = 1.301(6)$ Å, $R(N(2)—F(2)) = 1.265(9)$, and $R(N(2)—F(3)) = 1.321(10)$ Å; the F(1)—N(1)—F(1)

Table 2. Experimental frequencies (cm^{-1}) in vibrational spectra of $NF_4^+AuF_6^-$ and their assignment

Raman spectrum		IR spectrum (crystalline sample)	Frequency assignment and types of vibrations	
Crystalline sample	Solution in HF		$AuF_6^-(O_h)$	$NF_4^+(T_d)$
227 (43)	221 (34) p	—	ν_5 (F_{2g}), δ_s(F—Au—F)	—
442 (8)	437 (5) p	450 (vw)	—	ν_2(E), δ_s(F—N—F)
490 (<1)?	—	—	—	—
502 (<1)?	—	—	—	—
527 (6)	522 (4) p	—	ν_2(E_g), ν_s(Au—F)	—
596 (95)				
600 (100)	599 (100) p	—	ν_1(A_{1g}), ν_s(Au—F)	—
611 (14)	608 (sh) dp	610 (m)	—	ν_4(F_2), δ_{as}(F—N—F)
649 (≤1)	—	648 (vs)	ν_3(F_{1u}), ν_{as}(Au—F)	—
848 (12)	843 (9) p	—	—	ν_1(A_1), ν_s(N—F)
1074 (<1)?	—	—	—	—
—	—	1160 (s)	—	ν_3(F_2), ν_{as}(N—F)
—	—	1219 (w)	—	$2\nu_4$(A_1 + E + F_2)
—	—	1460 (w)	—	$\nu_1 + \nu_4$(F_2)

Note. Notations used here and in Tables 3—5 are as follows: ν is stretching, δ is deformation, s is symmetrical, as is antisymmetrical vibration; vs is very strong, s is strong, m is medium, w is weak, vw is very weak band; p is polarized and dp is depolarized line. For the Raman frequencies, listed are the corresponding line intensities in relative units.

angle is 108.5(3) and 111.5(5)°, the F(2)—N(2)—F(2) angle is 109.9(4), and the F(3)—N(2)—F(3) angle is 107.4(9)°.

A ^{19}F MAS NMR study[54] of the structure of $NF_4^+BF_4^-$ revealed that crystalline salt $NF_4^+BF_4^-$ contains only tetrahedral NF_4^+ cations and that the conclusion[52,53] about distortion of the tetrahedral structure of NF_4^+ was erroneous owing to incorrect interpretation of the results obtained. However, since information about nonequivalence of NF_4^+ cations was obtained[52,53] by X-ray analysis which gives the bond lengths and bond angles directly rather than indirectly, as ^{19}F MAS NMR spectroscopy, the conclusions[54] about the presence of only tetrahedral NF_4^+ in the crystalline salt $NF_4^+BF_4^-$ are doubtful.

We believe that no cation—anion interactions can occur in the $NF_4^+BF_4^-$ complex with a rather weak Lewis acid (BF_3). Therefore, the NF_4^+ cation can have a T_d-structure. At the same time, cation—anion interactions in the complex salts with AuF_5 (abnormally strong Lewis acid) may cause structural distortions in NF_4^+ as in the case of $ClF_2^+MF_6^-$ (M = Nb, Ta, Au) salts.[12,55]

Thus, the observed features of the vibrational spectrum of NF_4^+ cation as component of $NF_4^+AuF_6^-$ salt (the presence of "extra" lines in the Raman spectrum, the absence of vibrational bands for the T_d-structure allowed by the selection rules or, *vice versa*, the presence of corresponding bands forbidden by the selection rules, possible occurrence of noticeable cation—anion interactions affecting the N—F bond lengths in the $NF_4^+AuF_6^-$ cation) leave the problem of the structure of NF_4^+ as constituent of $NF_4^+AuF_6^-$ in the solid phase unsolved. We believe that detailed quantum chemical calculations of the geom-

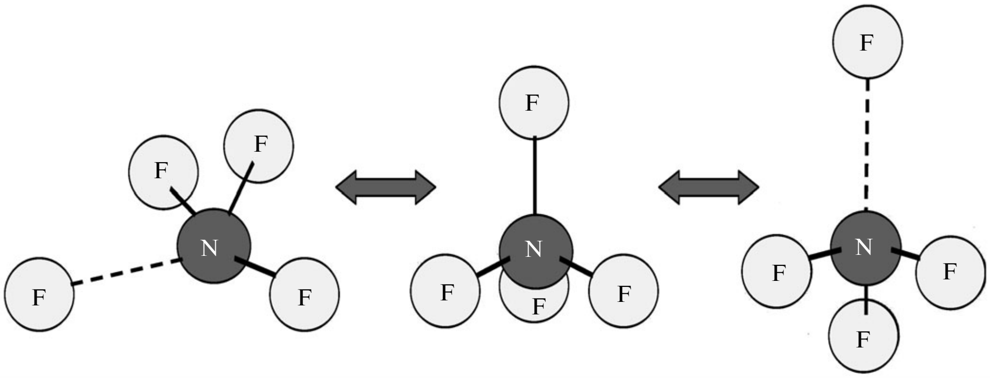


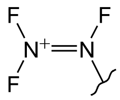
Fig. 2. Structural transformations $T_d \rightarrow C_{3v}$ or $T_d \rightarrow C_{2v}$ upon distortion of tetrahedral NF_4^+ cation.

etry of NF_4^+ cation, as well as studies on solid-state molecular geometry using new spectroscopic methods of investigation are on demand. These will allow one to study the formation of lines in the spectrum of this cation as a component of crystalline salt $NF_4^+AuF_6^-$ and its structure.

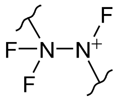
As to the AuF_6^- anion, the observed splitting of the $\nu_1(A_{1g})$ line can be due to slight tetragonal distortions of the O_h-structure of AuF_6^- in the anion lattice field, which lead to reduction of the anion symmetry owing to structural transformations $O_h \to D_{4h}$, $O_h \to C_{4v}$ *etc.* characteristic of some hexafluoro complexes.[56] This is also favored by the appearance of a $\nu_3(F_{1u})$ line of the vibration forbidden by the selection rules at about 650 cm^{-1} in the Raman spectrum. In addition, splitting of the ν_1 line (AuF_6^-) in the Raman spectra can be a consequence of manifestations of internal asymmetry of AuF_6^- owing to perturbative effect of excited electronic states with lower symmetry on the ground-state O_h symmetry.[51,56].

Compound $N_2F_3^+AuF_6^-$. Unlike NF_4^+ cation, data on the vibrational spectra of $N_2F_3^+$ cation first synthesized in 1965 [57] are scarce. There are only a few studies on the vibrational and NMR spectra of $N_2F_3^+$ cation as constituent of salts, namely, $N_2F_3^+XF_6^-$ (X = As, Sb), $N_2F_3^+SnF_5^-$, and $N_2F_3^+(SbF_6)_n^-$ (n = 2, 3).[58—60] According to the available spectroscopic data, planar (C_s) and nonplanar (C_1) structures of $N_2F_3^+$ cation are equiprobable; therefore, the assignment of the observed vibrational frequencies of $N_2F_3^+$ was the subject of a special discussion.[59,60]

Indeed, the $N_2F_3^+$ cation can be represented by two resonance structures (**I** and **II**) with different types of bonds between nitrogen atoms.



I (C_s)



II (C_1)

According to calculations,[50,61] the resonance structure **I** is energetically more favorable than structure **II**. Therefore, the assignment of vibrational frequencies of $N_2F_3^+$ cation as constituent of the $N_2F_3^+AuF_6^-$ salt was carried out for the planar C_s-structure similar to that of C_2F_4 molecule.[42]

Planar cation $N_2F_3^+$ (C_s) is characterized by nine IR and Raman active normal modes with the symmetry types $\Gamma_{vib} = 6\ A'$ (IR, Raman) + $3\ A''$ (IR, Raman). The modes belonging to the symmetry type A″ have higher depolarization ratios.

The vibrational frequencies of $N_2F_3^+AuF_6^-$ and $N_2F_3^+AuF_6^-$ in the solid state and in solution in HF are listed in Table 3. Frequency assignment in the spectra of $N_2F_3^+$ cation was based on the results of polarization measurements in the Raman spectrum of $N_2F_3^+AuF_6^-$ solutions in anhydrous HF and taking into account the published data[60] which seem to be quire reliable.

Eight vibrational bands are observed in the spectra of $N_2F_3^+$ (see Table 3). Bands in the region 300—700 cm^{-1} were assigned to the in-plane and out-of-plane deforma-

Table 3. Experimental frequencies (cm^{-1}) in vibrational spectra of $N_2F_3^+AuF_6^-$ and their assignment

Raman spectrum		IR spectrum (crystalline sample)	Frequency assignment and types of vibrations	
Crystalline sample	Solution in HF		$AuF_6^-(O_h)$	$N_2F_3^+(C_s)$
227 (43)	231 (35) p	—	ν_5 (F_{2g})	—
234 (sh)				
311 (6)	311 (4) p	—	—	$\nu_6(A')$, $\delta(FNNF_2)$ in-plane
499 (≤1)	496 (≤1) dp	495 (m)	—	$\nu_8(A')$, $\delta_s(FNNF_2)$ out-of-plane
521 (10)	518 (8) p	515 (m)	—	$\nu_5(A')$, $\delta_s(NF_2)$ in-plane
542 (5)	539 (4) p	—	$\nu_2(E_g)$	—
592 (66)	597 (100) p	—	$\nu_1(A_{1g})$	—
602 (100)				
659 (2)	—	650 (vs)	$\nu_3(F_{1u})$	—
673 (8)	670 (5) dp	669 (sh)	—	$\nu_7(A'')$, $\delta_{as}(FNNF_2)$ out-of-plane
926 (21)	923 (20) p	922 (m)	—	$\nu_4(A')$, $\nu_s(NF_2)$
998 (2)	992 (1) p	995 (w)	—	$2\nu_8(A')$
1125 (8)	1122 (5) p	1129 (s)	—	$\nu_3(A')$, $\nu_s(NF_2)$
1309 (3)	1305 (2) p	1312 (s)		$\nu_2(A')$, $\nu_{as}(NF_2)$
—	—	1342 (w)	—	$2\nu_7(A')$
—	—	1439 (vw)	—	$\nu_3 + \nu_6(A')$
1519 (4)	1517 (2) p	1523 (m)	—	$\nu_1(A')$, $\nu(N=N)$
—	—	1643 (w)	—	$\nu_3 + \nu_5(A')$
—	—	1976 (w)	—	$\nu_2 + \nu_7(A'')$
—	—	2231 (vw)	—	$\nu_2 + \nu_4(A')$

tion vibrations of $FNNF_2$ and NF_2 fragment (ν_5, ν_6, ν_7, ν_8). The bands corresponding to symmetrical (ν_3, ν_4) and antisymmetrical (ν_2) stretching vibrations and to the N=N stretching vibration (ν_1) appear at higher frequencies, namely, at 900—1500 cm^{-1}.

A characteristic feature of the spectra of $N_2F_3^+$ as constituent of the $N_2F_3^+AuF_6^-$ salt is the lack of the IR band corresponding to the ν_6(A´) vibration allowed by the selection rules and the appearance of IR bands assigned to compound vibrations and overtones of $N_2F_3^+$. Also, no band of the ν_9(A″) torsional vibration near 350 cm^{-1} was detected in our study, although it was observed[60] in the spectra of $N_2F_3^+$ as constituent of $N_2F_3^+XF_6^-$ (X = As, Sb) salts.

These features can be due to spectroscopic manifestations of structural nonrigidity by the mechanisms considered earlier,[12,62] in particular, by the mechanism of fast intramolecular exchange of F-ligands. In addition, they can be related to the formation of intermediate C_s-structure $F(1)NNF(2)_2$ with nonequivalent fluorine atoms; this structure is different from the resonance structures **I** and **II**. Such intermediate structures are formed in the course of *trans—cis*-isomerization of N_2F_2 molecules.[23]

The spectra of AuF_6^- anion exhibit splitting of the $\nu_1(A_{1g})$ and $\nu_5(F_{2g})$ lines and a line at 650 cm^{-1} corresponding to the $\nu_3(F_{1u})$ vibration forbidden by the selection rules. As in the case of $NF_4^+AuF_6^-$, this can be a consequence of (i) slight tetragonal distortions of the O_h-structure of AuF_6^- anion in the crystal field and (ii) manifestations of internal asymmetry of $N_2F_3^+AuF_6^-$. Taken altogether, these factors lead to symmetry reduction of AuF_6^- anion.

Compound $NOF_2^+AuF_6^-$. There are some studies on the vibrational and NMR spectra of NF_2O^+ cation as constituent of compounds $NF_2O^+BF_4^-$, $NF_2O^+B_2F_7^-$, $NF_2O^+XF_6^-$ (X = As, Sb), and $NF_2O^+Sb_2F_{11}^-$,[59,63,64] and on the crystal structure of some of these salts.[65] It was shown that the NF_2O^+ cation has a C_{2v}-structure with R(N—O) = 1.114 Å, R(N—F) = 1.284 Å, the F—N—F is 107.9°, and the O—N—F angle is 126.0°.[66]

The NOF_2^+ cation (C_{2v} symmetry) is characterized by six IR and Raman active normal vibrations with the symmetry types $\Gamma_{vib} = 3\ A_1$ (IR, Raman) + 2 B_1 (IR, Raman) + + B_2 (IR, Raman).

The vibrational frequencies of $NOF_2^+AuF_6^-$ in the solid state and in solution in HF are listed in Table 4. Frequency assignment in the spectra of NOF_2^+ cation was carried out based on the results of polarization measurements in the Raman spectrum of $NOF_2^+AuF_6^-$ solutions in anhydrous HF taking into account the interpretation of the vibrational spectrum of the isoelectronic analog COF_2 (see Ref. 42) and the assignment proposed in Ref. 64.

The vibrational spectrum of crystalline $NOF_2^+AuF_6^-$ (see Fig. 1) and its solution in HF exhibits all lines allowed by the selection rules for structures with the C_{2v} (NOF_2^+) and O_h (AuF_6^-) point symmetries.

A feature of the Raman spectrum of $NOF_2^+AuF_6^-$ is that, unlike the AuF_5 complexes considered above, the splitting of the $\nu_1(A_{1g})$ line for AuF_6^- anion and the $\nu_3(F_{1u})$ line forbidden by the selection rules are not observed, whereas the line $\nu_5(F_{2g})$ corresponding to a deformation vibration is split into three components. This may indicate weakening of cation—anion interactions in $NOF_2^+AuF_6^-$, so that distortion of the O_h-structure of AuF_6^- can mainly be due to the effect of the crystal field.[12,67]

Compound $NO^+AuF_6^-$. A number of studies describe the vibrational spectra of NO^+ cation as constituent of $NO^+XY_6^-$ (X = P, As, Sb; Y = F, Cl), $NO^+UF_7^-$, $(NO)_2^+UF_8^{2-}$, $NO^+BrF_4O^-$, $NO^+ZOF_5^-$ (Z = Mo, W,

Table 4. Experimental frequencies (cm^{-1}) in vibrational spectra of $NOF_2^+AuF_6^-$ and their assignment

Raman spectrum		IR spectrum (crystalline sample)	Frequency assignment and types of vibrations	
Crystalline sample	Solution in HF		$AuF_6^-(O_h)$	$NOF_2^+(C_{2v})$
224 (23)	221 (17) p	—	$\nu_5(F_{2g})$	—
232 (sh)				
239 (sh)				
537 (6)	532 (4) p	—	$\nu_2(E_g)$	—
576 (7)	572 (4) p	581 (s)	—	$\nu_3(A_1)$, δ_s(F—N=O) in-plane
600 (100)	596 (100) p	—	$\nu_1(A_{1g})$	—
632 (12)	627 (sh) dp	633 (sh)	—	$\nu_5(B_1)$, δ_{as}(F—N=O) in-plane
—	—	652 (vs)	$\nu_3(F_{1u})$	—
714 (2)	710 (1) dp	725 (m)	—	$\nu_6(B_2)$, δ(F—N=O) out-of-plane
897 (15)	895 (13) p	903 (s)	—	$\nu_2(A_1)$, ν_s(F—N)
1163 (≤1)	—	1148 (w)	—	$\nu_4(B_1)$, ν_{as}(F—N)
—	—	1237 (vw)	—	$2\nu_5(B_1)$
—	—	1792 (w)	—	$2\nu_1(A_1)$
1844 (≤1)	1848 (≤1) p	—	—	$\nu_1(A_1)$, ν(N=O)
1858 (≤1)	—	1869 (w)	—	—

Table 5. Experimental frequencies (cm^{-1}) in vibrational spectra of $NO^+AuF_6^-$ and their assignment

Raman spectrum		IR spectrum (crystalline sample)	Frequency assignment and types of vibrations	
Crystalline osample	Solution in HF		$AuF_6^-(O_h)$	$NO^+(C_{\infty v})$
229 (19)	225 (17)	—	$\nu_5(F_{2g})$	—
237 (sh)				
529 (5)	525 (4)	—	$\nu_2(E_g)$	—
591 (sh)	596 (100)	—	$\nu_1(A_{1g})$	—
601 (100)				
—	—	649 (s)	$\nu_3(F_{1u})$	—
2322 (sh)	2329 (13)	2324 (m)	—	$\nu(^1\Sigma^+)$, $\nu(N{\equiv}O)$
2329 (18)		1329 (sh)		

Cr), and $(NO)_2{}^+ZOF_6{}^{2-}$ (Z = Mo, W) salts[59,68–71] as well as their NMR spectra and crystal structures.[69,71,72] The synthesis of a $NOF \cdot AuF_5$ adduct was reported;[73] however, no vibrational frequency assignment was made.

Transformation of NOF molecule to NO^+ cation owing to a change in the atomic charge of oxygen having a higher electronegativity compared to nitrogen is accompanied by an increase in the nitrogen—oxygen bond order and in the ν(N—O) vibrational frequency. The effect of the change in charge (loss of an electron) on ν(N—O) is clearly seen in the series $NO^+ > NO > NO^- > NO^{2-}$.[42] The NO^+ cation has a $C_{\infty v}$ point symmetry and characterized by vibration of the N≡O triple bond (ground-state term $^1\Sigma^+$).[59,72]

The vibrational frequencies of $NO^+AuF_6^-$ in the solid state and in solution in HF are listed in Table 5. The data of Table 5 and Fig. 1 show that, similarly to the spectrum of $NOF_2{}^+AuF_6{}^-$, the vibrational spectrum of $NO^+AuF_6^-$ both in the crystalline phase and in solution in anhydrous HF includes all lines characteristic of the structures with $C_{\infty v}$ (NO^+) and O_h (AuF_6^-) symmetries and allowed by the selection rules. The ν(N≡O) band in the IR and Raman spectra is split into two components whose maxima are shifted by 10—15 cm^{-1} toward the long-wavelength region compared to the maximum of the corresponding band (~2340 cm^{-1}) in the spectra of $NO^+XF_6^-$ (X = As, Sb); no splitting of this band was observed.[59,70] Splitting of the ν(N≡O) band and its hypsochromic shift in both spectra can be due to the coexistence of two differently oriented crystalline modifications of the NO^+ cation in the $NO^+AuF_6^-$ salt in which the bond is somewhat longer owing to cation—anion interactions and the crystal field effect.[56,57]

As in the case of $NOF_2{}^+AuF_6{}^-$, the Raman spectrum of AuF_6^- shows no splitting of the $\nu_1(A_{1g})$ line and the $\nu_3(F_{1u})$ line forbidden by the selection rules. Doublet splitting of the $\nu_5(F_{2g})$ line is due to the same reasons as that observed for $NOF_2{}^+AuF_6{}^-$ (see above).

Summing up, the results obtained revealed the variety of spectroscopic manifestations of structural effects in gold pentafluoride complexes with nitrogen fluorides and oxofluorides. These features should be taken into account when using such compounds to solve fundamental and applied problems, in particular, in the synthesis of novel energetic materials.

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