Raman spectra and structural features of $ClOF_2^+$ cation in a solution of anhydrous HF

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The Raman spectra of $ClOF_2^+$ cation in solutions of anhydrous HF were studied. In the $ClOF_2^+HF_2^-$ and $ClOF_2^+BF_4^-$—HF systems, this cation exists as a pyramidal structure (C_s symmetry), while in the $ClOF_2^+AuF_6^-$—HF system, it exists as a planar structure (C_{2v} symmetry). Based on nonempirical calculations by the Hartree—Fock—Roothaan method, an explanation for the dependence of the structure of the $ClOF_2^+$ cation on the nature of the anion was proposed. For the Cl—O bond vibrations, the correlation functions of vibrational and rotational relaxations were calculated, and the characteristic times of these processes were determined. The main contribution to the formation of the band contours corresponding to the above-mentioned modes is made by the vibrational dephasing.

Key words: Raman spectrum, $ClOF_2^+$ cation, anhydrous HF, frequency of bond vibration, nonempirical calculations, Hartree—Fock—Roothaan method, correlation function, vibrational and rotational relaxations.

Chlorine oxyfluoride[1] has the pseudo-trigonal bipyramid (C_s symmetry) structure in which two F atoms occupy axial positions, while the third F atom, the O atom, and the lone electron pair are equatorial.[2] The bond lengths and bond angles assumed previously[2] for $ClOF_3$ (without experimental structural data) correspond to a regular C_s structure of the XYZ_3 type (trigonal bipyramid). However, the repulsion between the lone electron pair and the O atom, which forms a double bond with the Cl atom, should cause a substantial distortion of the regular trigonal-bipyramidal structure.[3] The structural parameters of the $ClOF_3$ molecule and the magnitude of its dipole moment (1.74 D), found by gas electron diffraction,[4] confirmed the occurrence of directed repulsion in the case of the double bond which has different populations of the π-binding orbitals in the equatorial and axial planes of the trigonal bipyramid.[5,6]

The presence of two highly polar Cl—F bonds in combination with low kinetic stability are responsible for the extremely strong oxidative properties of $ClOF_3$. In addition, $ClOF_3$ molecules are capable of forming complexes:

$$ClOF_3 + AF_n \rightleftharpoons [ClOF_2]^+[AF_{n+1}]^-, \quad (1)$$

$$ClOF_3 + BF_m \rightleftharpoons [ClOF_4]^-[BF_{m-1}]^+, \quad (2)$$

where AF_n and BF_m are Lewis acid and base, respectively, in a solution in anhydrous HF.[7] It has been noted[8,9] that the acid-base properties of amphoteric halogen fluorides can be revealed by comparing the structural stability of the initial molecule with that of the corresponding ion, which can be done using the data of vibrational spectroscopy.

Apparently, in addition to the structural features of a molecule, vibrational and rotational relaxation processes associated with the stochastic properties of its environment can substantially influence the parameters of a chemical reaction occurring in a highly polar solvent (like hydrogen fluoride[10]).[11] The required data on the change in the environment of a molecule under consideration can be obtained by investigating the correlation functions (CF).[12]

In this work, we studied the Raman spectra of the compounds formed from $ClOF_3$ in a solution in anhydrous HF; the dependence on the structure of the $ClOF_2^+$ cation on the nature of the anions was studied by quantum-chemical methods; the dynamic parameters of the cation in the $ClOF_2^+$—HF, $ClOF_2^+BF_4^-$—HF, and $ClOF_2^+AuF_6^-$—HF systems were determined.

Experimental

The Raman spectra of the $ClOF_2^+$—HF_2^-, $ClOF_2^+BF_4$—HF, and $ClOF_2^+AuF_6^-$—HF samples were recorded using an RTI-30 automated Raman spectrometer (Dilor) with a triple monochromator. The spectral width of the slits of the Raman spectrometer was maintained equal to 2.3 cm^{-1}. An LGN-503B argon laser with a power of up to 1 W with an excitation line at 488 nm was used as the source of excitation. The polarized and depolarized Raman spectra were recorded using a standard 90-degree geometry of the illumination of samples; prior to each subsequent recording of the spectrum, the polarization conditions varied randomly. The reproducibility of the frequencies corresponding to the maxima of the Raman lines was

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not worse than 0.4 cm^{-1}. The samples of $ClOF_3$—HF, $ClOF_2^+BF_4^-$—HF, and $ClOF_2^+AuF_6^-$—HF were placed into hermetically sealed transparent teflon tubes. The temperature of the samples was maintained constant (T = 293±2 K) using a water thermostat. All operations on the preparation of the samples were carried out under dry argon. The accuracy of determination of the concentrations of $ClOF_3$, $ClOF_2^+BF_4^-$, and $ClOF_2^+AuF_6^-$ in HF solutions amounted to 5—10 rel.%. The samples of $ClOF_3$ used to record its Raman spectra and to prepare its salts were at least 99% pure, and HF was thoroughly purified and dried. The degree of drying of HF was monitored based on the absorption bands in the H_2O vibration region in the IR spectrum using the procedure described previously.[13] A cell with a controlled thickness, specially developed based on KRT-2 for aggressive liquid media, was used to record the spectra.

The accuracy in the determination of the line maxima and their full widths at half-height in the Raman spectra was at least 1 cm^{-1}.

Calculation Procedure

The spectra of isotropic and anisotropic scattering, the correlation functions, and the corresponding times of vibrational and orientational relaxations were calculated on an IBM PC/AT using a specialized program.

Quantum-chemical calculations were carried out by the Hartree—Fock—Roothaan (HFR) method using the MICROMOL program,[14] which was adapted for IBM PC/AT/486. In most calculations, we used the expanded valence-two-exponent 6-31G Pople basis set (see, for example, Ref. 15) supplemented by a polarization function on the central atom (the 6-31G* basis set) and by the diffusion function on the F atoms (the 6-31+G* basis set). The exponents of the polarization p- and d-functions for the H and B atoms were found from the condition of the minimized total energies of the HF and BF_3 molecules at their equilibrium (known from experiments)[16] geometries; $\alpha_p(H)$ = 0.9515 and $\alpha_d(B)$ = 0.6421, respectively. The exponent of the polarization d-function on the Cl atom was taken to be $\alpha_d(Cl)$ = 0.75.[14] The exponent of the diffuse p-function on the F atoms ($\alpha_p(F)$ = 0.10) was found by minimization of the total energy of the F^- ion.

For the $ClOF_2^+$ cation, we also carried out more precise calculations with a fuller McLean—Chandler—Husinaga—Dunning two-exponent basis set, $(12s9p/6s4p)_{Cl}$[17] + $(9s5p/4s2p)_{O,F}$,[18,19] supplemented by the polarization d-function on the Cl atom with the standard exponent $\alpha_d(Cl)$ = 0.68 (the DZ+P basis set). In the case of FHF^- anion ($D_{\infty h}$ symmetry), the refinement was carried out with the Husinaga—Dunning two-exponent basis set, $(9s5p/4s2p)_F$ + $(4s/2s)_H$,[18,19] supplemented by the polarization p-function on the H atom and by the polarization d-function and diffuse p-function on the F atoms (the DZ+2P+DF basis set). In this case, the exponent of the polarization p-function on the hydrogen atom $\alpha_p(H)$ = 0.7147 was optimized using the total energy of the HF molecule at its equilibrium (found by calculations) internuclear distance, R = 0.906 Å, while the exponents of the polarization d-function and diffuse p-function on the fluorine atom ($\alpha_d(F)$ = 1.4433, $\alpha_p(F)$ = 0.0763) were optimized using the total energy of F^- ion.

Full optimization of geometric parameters of the molecular systems under study was carried out with all the above-indicated basis sets at a convergence threshold with respect to the energy gradient of 10^{-4} au. Comparative nonempirical studies performed with different basis sets showed that calculations with the 6-31G* and 6-31+G* basis sets reproduce the results of more precise calculations with an accuracy of 0.04 Å for internuclear distances and 3° for bond angles, and also reproduce the experimental structural data for the $ClOF_3$ molecule (C_s symmetry) and for the $ClOF_2^+$ cation in the pyramidal configuration. In addition, calculations with the 6-31+G* basis set reproduce the results of more precise calculations of the energy effects of the reactions considered with an accuracy of 4 kcal mol^{-1}. Therefore, in general, the 6-31+G* basis set can be chosen as the optimum for semiquantitative description of the complex formation.

Results and Discussion

Raman spectra of the $ClOF_2^+$ cation in solutions of anhydrous HF. The Raman spectra of the $ClOF_2^+$ cation in the solid state and in HF solutions ($ClOF_2^+PF_6^-$, $ClOF_2^+UF_6^-$,[20] $ClOF_2^+SbF_6^-$, $ClOF_2^+AsF_6^-$, $ClOF_2^+BF_4^-$, $ClOF_2^+HF_2^-$,[21] $ClOF_2^+PtF_6^-$, $ClOF_2^+BF_4^-$, $ClOF_2^+AsF_6^-$ [22]) have been studied previously; however, the structure of this cation has not been determined. It has been suggested[22] that the $ClOF_2^+$ cation has a pyramidal structure characterized by the C_s point group of symmetry, although some of the spectroscopic data point to a planar C_{2v} configuration. It should be noted that vibrational spectra of molecules of the XYZ_2 type with C_s or C_{2v} symmetry are almost indistinguishable. In both cases, all six vibrations are active both in the IR and Raman spectra. A difference can be observed only in the polarized Raman spectra; in this case, the spectrum of an XYZ_2 molecule with C_s symmetry exhibits four polarized lines, whereas the spectrum of an XYZ_2 molecule with C_{2v} symmetry contains only three lines.

In order to determine the structure of the $ClOF_2^+$ cation, we carried out precision polarization measurements of the Raman spectra of chlorine oxytrifluoride and two of its salts in anhydrous HF at various concentrations of the solutions: $ClOF_3$ (C = 1.8—9.2 mol L^{-1}), $ClOF_2BF_4$ (C = 1.3—2.9 mol L^{-1}), and $ClOF_2AuF_6$ (C = 0.3—2.6 mol L^{-1}).

The Raman spectra of the $ClOF_3$—HF and $ClOF_2BF_4$—HF systems exhibit four polarized lines corresponding to the ν_1, ν_2, ν_3, and ν_4 symmetrical stretching and deformation modes of the pyramidal $ClOF_2^+$ cation (Table 1). However, the Raman spectrum of the $ClOF_2AuF_6$—HF system contains three polarized bands due to the ν_1, ν_2, and ν_3 modes of the $ClOF_2^+$ cation having a planar structure.

Initially, the dependence of the structure of the $ClOF_2^+$ cation on the nature of the anion has been attributed to its possible stereochemical flexibility with respect to inversion, similar to the flexibility observed for NH_3 molecule. However, the nonempirical calculations that we carried out with the 6-31G* basis set showed that the energy of the planar C_{2v} configuration of a separate $ClOF_2^+$ cation is 62 kcal mol^{-1} larger than the energy of the pyramidal C_s configuration. Calculations

Table 1. Experimental frequencies (ν/cm^{-1}) and band half-widths (Γ/cm^{-1}) in the Raman spectra of the $ClOF_2^+$ in the $ClOF_3$—HF, $ClOF_2BF_4$—HF, and $ClOF_2AuF_6$—HF systems

$ClOF_3$—HF		$ClOF_2BF_4$—HF		$ClOF_2AuF_6$—HF		Vibrational mode	Assignment
ν	Γ	ν	Γ	ν	Γ		
1333 p	9.9	1334 p	8.1	1338 p	6.5	$\nu_1(A')$	$\nu(Cl—O)$
1321 p	10.1	1322 p	8.5	1327 p	7.0		
736 p	30.3	742 p	22.3	748 p	15.2	$\nu_2(A')$	$\nu_s(Cl—F)$
705 dp	19.6	711 dp	14.1	714 dp	9.9	$\nu_5(A'')$	$\nu_{as}(Cl—F)$
512 p	10.5	513 p	8.5	502 p	6.0	$\nu_3(A')$	$\delta_s(Cl—F)$
403 dp	17.1	404 dp	10.0	397 dp	8.0	$\nu_6(A'')$	$\delta_{as}(Cl—F)$
387 p	11.9	386 p	6.8	380 dp	5.7	$\nu_4(A')$	$\delta_s(F—Cl—O)$

Notation: p is polarized, dp is depolarized, ν is stretching, and δ is deformation vibrations.

with the fuller DZ+P basis set gave an almost identical barrier to the inversion of the cation (58 kcal mol^{-1}). In addition, calculations with both basis sets predict a T-shaped structure of the planar $ClOF_2^+$ cation, which resembles the known (see, for example, Ref. 7) unique structures of the interhalogen molecules ClF_3 and BrF_3. The F—Cl—F bond angle is equal to 175° irrespective of the basis set used; the Cl—F bond length is 1.63 Å (the 6-31G* basis set) or 1.64 Å (the DZ+P basis set), and the Cl—O bond length is 1.43 Å (the 6-31G* basis set) or 1.44 Å (the DZ+P basis set).

The calculations of the geometric structure of the $ClOF_3$ molecule (C_s symmetry) carried out with the 6-31G* basis set indicate that the structure of the $ClO(F_{ax})_2$ fragment in this molecule coincides with that of the planar $ClOF_2^+$ cation to within 0.07 Å for internuclear distances and to within 7° for bond angles. The analogy between the geometries of the pyramidal $ClOF_2^+$ cation and the $ClOF_{ax}F_{eq}$ structural fragment in the $ClOF_3$ molecule (to within 0.12 Å and 14°, according to calculations with the 6-31G* basis set, and to within 0.09 Å and 13°, according to experimental structural data for the $ClOF_3$ [4] molecule and the pyramidal $ClOF_2^+$ cation[22]) is also significant. The above-noted structure preservation of the fragments of the planar and pyramidal $ClOF_2^+$ cations incorporated into a chlorine oxytrifluoride molecule suggests the following scheme for the formation of ionic complexes of the $ClOF_2^+$ cation with $[AF_{n+1}]^-$ anions (AF_n = HF, BF_3, AuF_5). The $ClOF_3$ molecule reacts with the Lewis acids HF or BF_3 *via* its axial F ligand to give complexes $[ClOF_2]^+(C_s)\cdot[AF_{n+1}]^-$ in which the cation is pyramidal, whereas the abnormally strong Lewis acid AuF_5 [10] adds to the $ClOF_3$ molecule *via* the equatorial F ligand to give ionic complex $[ClOF_2]^+(C_{2v})\cdot[AF_6]^-$ in which the cation is planar.

The estimates of the heats of gas-phase reaction (1) made by nonempirical calculations with the 6-31+G* basis set (without allowance for the solvation effects) can serve as additional evidence supporting this mechanism. From the energy diagram of complex formation (Fig. 1), it follows that the energy of the formation of an isolated ion pair from the planar $ClOF_2^+$ cation (C_{2v} symmetry) and linear FHF^- anion ($D_{\infty h}$ symmetry) amounts to 227 kcal mol^{-1} and decreases to 182 kcal mol^{-1} on passing to the tetrahedral BF_4^- anion (T_d symmetry). In the case of the octahedral AuF_6^- anion (O_h symmetry), the energy required for the formation of an ionic pair with the planar $ClOF_2^+$ cation is less than 124 kcal mol^{-1} (see Fig. 1, *c*). In the latter case, the energy of the addition of the F^- ion to AuF_5 was estimated using the calculated[23] vertical electron affinity (EA) of the $AuF_6^{\cdot}$ radical, equal to 8.1 eV. However, in the description of the formation of AuF_6^- from neutral $AuF_6^{\cdot}$ radical, it is necessary to take into account the structural relaxation of the anion resulting from the addition of an electron to the radical, *i.e.*, to introduce the adiabatic correction. The calculations with the most accurate basis set, DZ+2P+DF, showed that for the FHF^- anion, this correction is equal to +0.9 eV, whereas calculations with the working 6-31+G* basis set lead to an adiabatic correction for the BF_4^- anion of +1.6 eV. Obviously, the magnitude of this correction would be even larger in the case of the AuF_6^- anion, because this system possesses more degrees of freedom for structural relaxation than those considered above. According to our estimates, the adiabatic EA for the $AuF_6^{\cdot}$ radical is higher than 9.7 eV. The adiabatic EA of $AuF_6^{\cdot}$ consists of the EA of the F atom (3. 4 eV [24]) and the energy of addition of F^- to AuF_5 minus the energy of addition of the F atom to $AuF_5^{\cdot}$. The latter energy contribution can be neglected, because for $AF_{n+1}^{\cdot}$ radicals, it is less than 0.1 eV (for example, according to our calculations with the DZ+2P+DF basis set, the energy of interaction of a F atom with an HF molecule is 0.03 eV). Our estimates showed that the energy of the $F^- + AuF_5^{\cdot} \rightarrow AuF_6^-$ process is higher than 145 kcal mol^{-1} (see Fig. 1, *c*).

As shown above, the energy spent for the formation of an isolated ion pair "planar $ClOF_2^+$ cation—$[AF_{n+1}]^-$ anion" decreases monotonically in the series of anions FHF^-, BF_4^-, AuF_6^-. In the case of the two former anions, formation of the $[ClOF_2]^+(C_{2v})\cdot[AF_{n+1}]^-$ ionic complex containing a planar cation is energetically unfavorable; only ionic complexes with pyramidal cations are formed. According to Fig. 1, *a*,*b*, the

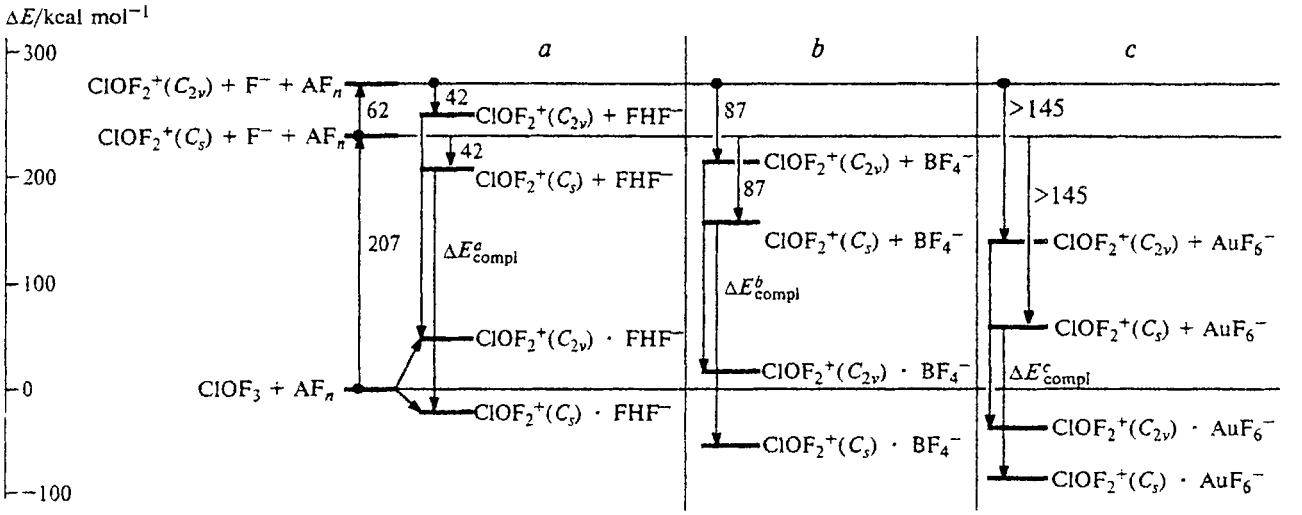

Fig. 1. Energy diagram found by *ab initio* calculations with the 6-31+G* basis set for the complexation process according to the equation $ClOF_3 + AF_n \rightleftharpoons [ClOF_2]^+[AF_{n+1}]^-$, where AF_n = HF (*a*), BF_3 (*b*), AuF_5 (*c*).

$[ClOF_2]^+(C_s) \cdot [AF_{n+1}]^-$ complex is formed if the following conditions are satisfied (E/kcal mol^{-1}): $165 < \Delta E_{compl} < 227$ (*a*) and $120 < \Delta E_{compl} < 182$ (*b*).

Conversely, in the case of the AuF_6^- anion, formation of ionic complexes with both planar and pyramidal structures of the cation become energetically favorable (see Fig. 1, *c*). However, the formation of the $[ClOF_2]^+(C_s) \cdot [AF_{n+1}]^-$ ionic complex, which is the most favorable from the energy viewpoint, is hampered, apparently, for kinetic reasons. Meanwhile, the pathway to complexes with the planar $ClOF_2^+$ cation has no activation barrier.

The use of highly polar solvents results in a decrease in the energy effects of complexation, while the planar structure of the $ClOF_2^+$ cation is stabilized in the additional strong field of the AuF_6^- anion. Note that the fact that internuclear distances for the C_s and C_{2v} configurations of the $ClOF_2^+$ cation coincide (within the errors of calculations with the 6-31G* and DZ+P basis sets) is in agreement with the fact that vibration frequencies for these configurations differ only slightly (by no more than 12 cm^{-1}) (see Table 1).

The spectroscopic and quantum-chemical results indicate that the character of interaction of the abnormally strong Lewis acid AuF_5 with $ClOF_3$ in the presence of HF differs crucially from that for the weaker Lewis acids HF and BF_3. The complexation of AuF_5 with $ClOF_3$ occurs with participation of the equatorial F atom of the $ClOF_3$ molecule, whereas the reactions with HF and BF_3 involve solely axial F atoms. The strong field of the AuF_6^- anion in combination with the field of the solvent accounts for the structural flexibility of the $ClOF_2^+$ cation; consequently, it assumes a T-shaped planar configuration.

It follows from Table 1 that the $\nu_1(A')$ line of $ClOF_2^+$ is split into two components; this has also been observed[25] for its isoelectronic analog SOF_2. This splitting is due to the Fermi resonance between the $\nu_1(A')$ mode and the $\nu_2+\nu_3(A')$ compound mode (for SOF_2, ν_1 = 1339; 1329 cm^{-1}, ν_2 = 808 cm^{-1}; ν_3 = 530 cm^{-1} [25]). The frequency of the $\nu_2+\nu_3$ compound mode of the $ClOF_2^+$ cation, unlike that of SOF_2, is lower than the frequency of $\nu_1(A')$ by 60—80 cm^{-1}; therefore, the contribution of the Fermi resonance to the splitting of the ν_1 line of $ClOF_2^+$ should be relatively small. It is more likely that the spitting is due to the fact that vibrations of the Cl—O bond in the two isotope modifications ($^{35}ClOF_2^+$ and $^{37}ClOF_2^+$) are observed in the Raman spectra of the $ClOF_2^+$ cation. According to our estimates, the isotope shift $\Delta\nu_1$ amounts to ~12 cm^{-1}.

Dynamics of the $ClOF_2^+$ cation in a solution of anhydrous HF. The vibrational and rotational CF ($G_V(t)$ and $G_R(t)$, respectively) were found using two procedures:[12] (1) Fourier transform of the Raman band contours found experimentally (the discrete Fourier transform); (2). Simulation of the Raman band contours by an analytical function and subsequent application of the Fourier transform assuming that the Raman band contours can be described by a symmetrical curve of the Lorentzian type.

The contour of the Raman band corresponding to the $\nu_1(A')$ vibration of the $ClOF_2^+$ cation with a frequency of 1300 cm^{-1} served as the experimental base for the calculation of CF. The typical shapes of the vibrational and rotational CF for ν_1 of $ClOF_2^+$ are shown in Fig. 2. The time variation of the correlation functions indicates that the contour of the corresponding band is formed almost entirely by the vibrational relaxation process. This is also indicated by the times of vibrational (τ_V) and rotational (τ_R) relaxations calculated assuming that the CF for the real and simulated (Lorentzian) band contours are close to each other

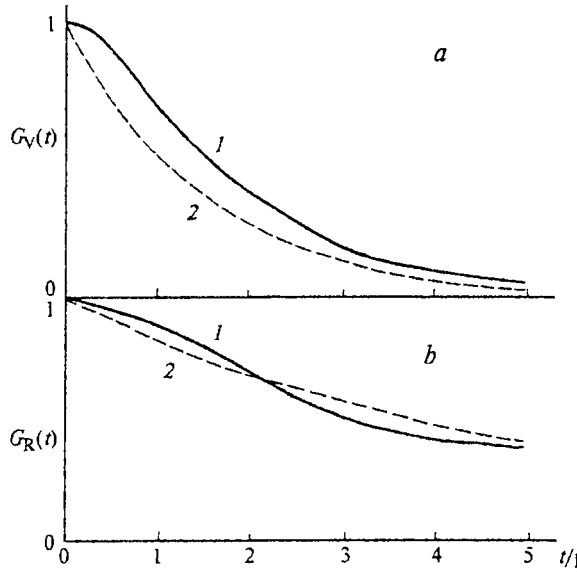

Fig. 2. Vibrational (*a*) and rotational (*b*) CF calculated by the Fourier transforms of the experimental (*1*) and simulated (*2*) band contours of the $\nu_1(A')$ mode of the $ClOF_2^+$ cation in the $ClOF_3$—HF system at C = 5.0 mol L^{-1}.

(Table 2). It follows from Table 2 that the rate of failure of the vibration phase is much higher than the reorientation rate and, therefore, the process of formation of the $\nu_1(A')$ contour for the $ClOF_2^+$ cation can be regarded as a manifestation of pure dephasing of this vibration. In addition, it can be seen from Table 2 that an increase in the concentration of $ClOF_2^+$ results in a slight decrease in the time of vibrational relaxation, whereas the rotational relaxation time remains virtually constant. This fact can be interpreted in the following way. In the liquid state, HF molecules normally exist as zigzag-shaped chains.[26] When a polymeric species $(HF)_n$ (n = 6—7) collides with the $ClOF_2^+$ cation, the vibration energy would be distributed more likely among the identical HF molecules incorporated in the chain than between the $ClOF_2^+$ cation and individual molecules in the chain. As the concentration of the $ClOF_2^+$ cations increases, the probability of their collisions with one another increases; this leads to efficient exchange by vibrational energy resulting in acceleration of vibrational relaxation. In addition, some decrease in the time of vibrational relaxation following an increase in the concentration of $ClOF_2^+$ in solution may be due to enhancement of the interaction of anions with $ClOF_2^+$; this, in turn, can markedly increase the probability of formation of ion pairs. This assumption is quite consistent with the views developed previously[27,28] in relation to concentrated aqueous solutions of nitrates and thiocyanates, which contain a diversity of species (contact ion pairs and more complex aggregates) arising due to strong interactions.

The rotational relaxation is mostly due to the fact that rotation of the $ClOF_2^+$ cations is hindered by

Table 2. Times of vibrational (τ_V) and rotational (τ_R) relaxation of the $ClOF_2^+$ cation in the $ClOF_3$—HF, $ClOF_2BF_4$—HF, and $ClOF_2AuF_6$—HF systems

System	C/mol L^{-1}	τ_V/ps	τ_R/ps
$ClOF_3$—HF	2.2	1.62±0.15	5.63±0.30
	5.0	1.43±0.10	5.91±0.25
	7.9	1.21±0.05	5.38±0.15
$ClOF_2BF_4$—HF	1.5	1.57±0.20	6.67±0.30
	2.1	1. 42±0.10	6.24±0.25
	2.8	1.23±0.05	6.92±0.20
$ClOF_2AuF_6$—HF	0.5	2.05±0.25	14.55±0.45
	1.4	1.84±0.15	15.12±0.30
	2.3	1.70±0.10	14.70±0.20

collisions with associated $(HF)_n$ molecules. Since the frequency of these collisions practically does not depend on the concentration of $ClOF_2^+$ cations, it should be expected that the time of rotational relaxation also would not depend on the concentration of chlorine oxydifluoride in HF. The rotational relaxation time τ_R in the $ClOF_2^+AuF_6^-$—HF system is 7—9 times larger than the vibrational relaxation time τ_V, whereas in the case of the $ClOF_3$—HF and $ClOF_2^+BF_4^-$—HF systems, the τ_R/τ_V ratio is 4—6, apparently, due to the transformation of the $ClOF_2^+$ structure.

For all three systems under consideration, correlation functions were calculated within the limits of fast and slow modulations (Fig. 3). In the case of the $ClOF_3$—HF system (see Fig. 3, *a*) at $t \leq 1.5$ ps, the slow modulation mechanism predominates, whereas for larger t values ($t \geq 3.0$ ps), uniform broadening is observed. A similar type of broadening characterizes the $ClOF_2BF_4$—HF system (see Fig. 3, *b*) with the only difference being that the mechanism of nonuniform broadening acts at $t \leq 0.4$ ps, whereas the effect of fast modulation is manifested at $t \geq 2.5$ ps. In the $ClOF_2AuF_6$—HF_2 system, slow modulation predominates at $t \leq 0.3$ ps, and the transition to the fast modulation mechanism occurs at $t \approx 1.0$ ps (Fig. 3, *c*).

The character of vibrational correlation functions found within the limits of fast and slow modulations indicates that the $ClOF_3$—HF system is the most sensitive to the behavior of neighboring species. Conversely, the $ClOF_2AuF_6$—HF system experiences the minimum perturbation caused by the local environment, which serves as additional evidence for the strong influence of the field of the AuF_6^- anion on the $ClOF_2^+$ cation.

Thus, the combination of the spectroscopic, quantum-chemical, and dynamic data obtained makes it possible to conclude that the complexation of $ClOF_3$ with Lewis acids of the AF_n type can follow two pathways, namely, it involves the axial F atoms in the case of HF or BF_3 and the equatorial F atom in the case of the abnormally strong Lewis acid AuF_5. When the process occurs by the second pathway, the effects of the fields of

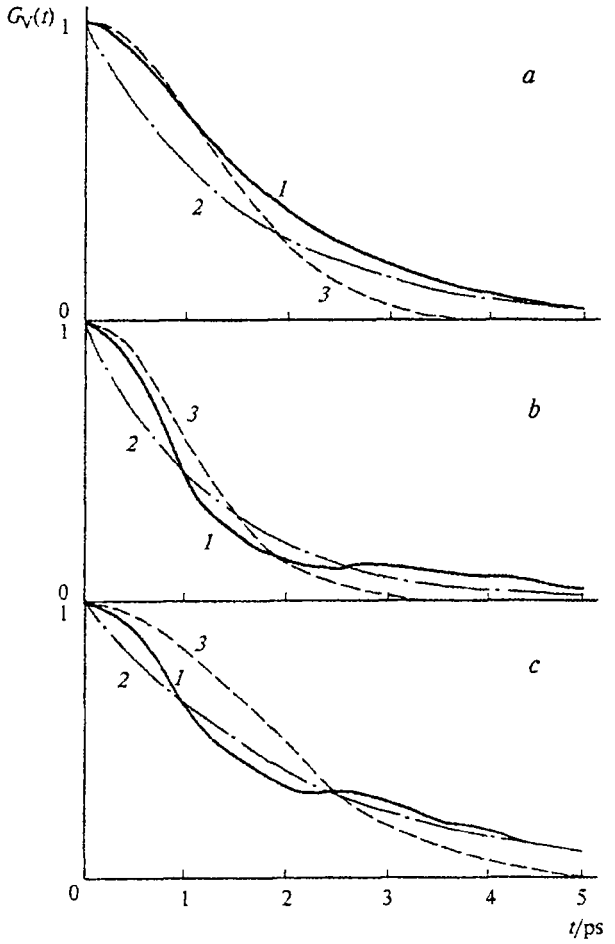

Fig. 3. Vibrational CF $G_V(t)$ for the $\nu_1(A')$ mode of the $ClOF_2^+$ cation (*1*) and the limiting dependences of $G_V(t)$ for fast (*2*) and slow (*3*) modulation in the $ClOF_3$—HF (*a*), $ClOF_2BF_4$—HF (*b*), and $ClOF_2AuF_6$—HF (*c*) systems at C = 5.4, 2.1, 1.7 mol L^{-1}, respectively.

the AuF_6^- anion and the solvent induce the structural transition of the $ClOF_2^+$ anion to a unique T-shaped planar configuration, which is known only for ClF_3 and BrF_3. The results obtained here make it possible to predict the behavior of $ClOF_3$ molecules in various physicochemical processes both in the gas and condensed phases as well as in the synthesis of new power-consuming binary and complex compounds containing halogen and oxygen atoms.

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