

## SPECTROCHEMICAL ASPECTS OF REMOTE LASER MONITORING OF EMERGENCY EMISSIONS FROM PLANTS WITH NUCLEAR FUEL CYCLE

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*Main stages of a nuclear fuel cycle (NFC) are considered in the paper. A short list of radioactive and toxic compounds is presented as possible components of an emergency emission at each stage of the NFC. The vibrational spectra of the uranium fluorides and oxifluorides and the elements from chromium subgroup in various aggregate states have been studied. The main chemical processes in the atmosphere with the uranium fluorides and oxifluorides participation have been analyzed as well as their influence on the vibrational spectra of the pointed compounds. It is shown that a structurally nonrigid molecular complex with general formula  $(\text{HF})_n \cdot (\text{H}_2\text{O})_m$ , ( $n, m \geq 2$ ) is formed as the result of the HF and  $\text{H}_2\text{O}$  molecules interaction, characterized by several types of motions of large amplitude, the spectrum of which may significantly differ both from the pure HF and  $\text{H}_2\text{O}$  spectra and from spectra of the well-known complex  $\text{HF} \cdot \text{H}_2\text{O}$ .*

The problems of expeditious control over gaseous and aerosol emissions from the plants of nuclear fuel cycle are now growing in importance in connection with their deteriorative action on the environment accompanied by an increasing anxiety of the population. First of all, the question is in possible after-effects of the emergencies at such plants caused by emissions of radio-active materials<sup>1</sup> and different toxic compounds.<sup>2</sup>

The methods of remote laser sounding<sup>3</sup> are now the most promising for real-time obtaining of reliable information on the concentration and chemical (molecular) composition of the ejected matter. These methods, in turn, require a detailed information on vibrational spectra of the emitted radioactive and toxic components under condition of their active interaction with water vapors and some atmospheric gases.

Main stages of the NFC are treated in this paper from the standpoint of possible emergencies. Also investigated are the IR-spectra of the uranium fluorides ( $\text{MF}_4$  and  $\text{MF}_6$ ) and oxifluorides ( $\text{MOF}_4$  and  $\text{MO}_2\text{F}_2$ ) and the elements from chromium subgroup in gas phase ( $T = 293$  K), solid state ( $T = 150-283$  K), in conditions of matrix isolation ( $T = 10-20$  K), and in solutions of liquefied Kr and Xe ( $T = 120-200$  K). The particular attention is paid to possible transformations of the vibrational spectra of these molecules due to formation of stable molecular complexes and hydrates in interaction with atmospheric moisture as well as to the spectra of their hydrolysis products.

The NFC typically includes the following main stages: hydrometallurgical production and refining of the primary nuclear fuel, fabrication of  $\text{UF}_4$  and  $\text{UF}_6$ ,

isotope enrichment of uranium, fabrication of fuel elements, and radiochemical production. The conducted analysis has shown that an emergency can take place practically at each stage of the NFC.

At the stage of the uranium ore processing by means of oxidizing and subsequent acidic or carbonate leaching, an emission of the uranium sulfate or phosphosulfate solutions and the accompanying components of raw materials may occur.

The ejections of organic extractants (alkyl phosphoric acid, amines, heavy hydrocarbons such as kerosene and dodecane, etc.) as well as the nitrate solutions, including the uranium, plutonium and some other actinides and fission products may happen during the uranium refining stage.

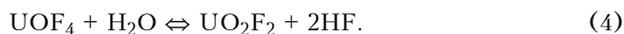
At the next stages of the NFC, the emergency emissions of the uranium tetrafluorides and hexafluorides; high-toxic hydrofluoric acid; volatile fluorides from the chromium subgroup inherent in the exhausting gases; nitric acid; gaseous fission products (ruthenium oxide, tritium,  $^{131}\text{I}$ ,  $^{85}\text{Kr}$ ,  $^{133}\text{Xe}$ , etc.); components of borosilicate and phosphate glass used in vitrification of highly active nuclear waste, and so on, may take place. This is not at all the complete list of the compounds, which can be a part of an emergency emission from the NFC plants. Note, that because of the necessity to recover the armament plutonium liberated as the result of the strategic offensive armament reduction, a proper allowance must be made for possible emergency in the process of mixed oxide fuel fabrication (MOX-fuel) rich in  $^{241}\text{Am}$ ,  $^{242}\text{Cm}$ , and other isotopes of transplutonium elements.

Evidently, that the significantly higher (comparative to the fuel made of  $\text{UO}_2$ ) concentration of  $^{238}\text{Pu}$ ,  $^{241}\text{Pu}$ , and  $^{242}\text{Pu}$  in the MOX-fuel is responsible for much higher level of the radioactive hazard. Therefore the manufacturing processes dealing even with "pure" plutonium (free of fission products activity) require special precautions for remote servicing and control.

One of the most dangerous components of an emergency at the NFC plants is the volatile  $\text{UF}_6$  being the most chemically active compound from all known uranium fluorine-containing compounds. According to its reactivity it is between actinide hexafluorides and the elements from chromium subgroup<sup>4</sup>



In the case of the emergency the uranium hexafluoride actively interacts with atmospheric moisture. This results in formation of  $\text{UO}_2\text{F}_2$  and  $\text{UOF}_4$  disproportionated to uranyl-fluoride. The process of the uranium hexafluoride hydrolysis may be expressed through the following equations:



On interaction of the  $\text{UF}_6$  or  $\text{UO}_2\text{F}_2$  with the atmospheric hydrogen, a reduction of the uranium hexafluoride to nonvolatile uranium tetrafluoride with its further hydrolysis may take place as well as a reduction of the uranium dioxydyfluoride to nonvolatile uranium dioxide:



According to the data from Ref. 5, the reactions (2) and (5) are exothermic and may proceed (particularly at high enough temperatures) with significant decrease of the Gibbs energy magnitude. The feature of the  $\text{UF}_6$  hydrolysis is the fact, that its participants are the covalent ( $\text{UF}_6$ ) and ionic ( $\text{UF}_4$  or  $\text{UO}_2\text{F}_2$ ) uranium fluorides and oxifluorides and the hydrolysis process includes both homogeneous ((2) and (5)) and heterogeneous ((6) and (7)) stages. It essentially complicates the instrumentation and the conducting of the spectroscopic experiments under conditions simulating the atmospheric ones. Besides the atmospheric moisture, the uranium hexafluoride may react with gaseous components of the emergency emission and some atmospheric gases such as organic compounds, hydrocarbons, amines, carbonic acid, etc., what results in formation of  $\text{NH}_4\text{UF}_5$ , ammonium fluoride, carbonyl fluorides, HF, and so on.

Taking into account that the most hazardous elements of the emergency emissions at the NFC plants are the uranium tetrafluoride and hexafluoride and the main products of their hydrolysis are the uranium

oxitetrafluoride and dioxydyfluoride, let us observe more attentively the vibrational spectra of the molecules  $\text{UF}_4$ ,  $\text{UF}_6$ ,  $\text{UOF}_4$ ,  $\text{UO}_2\text{F}_2$  and as well the spectra of isoelectric fluorides and oxifluorides of the elements from chromium subgroup  $\text{MF}_6$  ( $M = \text{Mo}, \text{W}$ ),  $\text{MOF}_4$  ( $M = \text{Cr}, \text{Mo}, \text{W}$ ),  $\text{UO}_2\text{F}_2$  ( $M = \text{Cr}, \text{Mo}$ ) in various aggregate states.

Table I presents the parameters of the vibrational bands of the Xe natural composition in the gaseous and liquid phases within the IR spectra of the  $\text{UF}_6$  (the advantages of methods of the cryogenic spectroscopy over the gas IR-spectroscopy ones are well-known<sup>6,7</sup>).

Our estimates of the integral absorption coefficient of  $\text{UF}_6$  molecule, placed into liquid xenon, have shown the obtained value  $A = 440 \pm 60 \text{ cm}^2 \cdot \text{molec}^{-1} \cdot \text{s}^{-1}$  for the band of antisymmetric valence vibration  $\nu_3(\text{F}_{1u})$  to agree well with the data from Ref. 8. These data were obtained from the IR-spectra of gaseous  $\text{UF}_6$  using the diode laser ( $\Delta\nu = 10^{-4} \text{ cm}^{-1}$ ) and the multipass cell with  $L = 80\text{--}400 \text{ m}$  at the  $\text{UF}_6$  vapors pressure  $P = 10^{-1}\text{--}10^{-3} \text{ Torr}$ . The values of  $A$  for the transition bands of the second order with the quantum  $\nu_3$  participation are within the limits  $(1.0\text{--}0.20) \cdot 10^{-8} \text{ cm}^2 \cdot \text{molec}^{-1} \cdot \text{s}^{-1}$ , and the same value for the transition bands of the third order is within the limits  $(0.02\text{--}0.01) \cdot 10^{-8} \text{ cm}^2 \cdot \text{molec}^{-1} \cdot \text{c}^{-1}$  (see Ref. 9).

TABLE I. Frequencies ( $\nu$ ,  $\text{cm}^{-1}$ ), halfwidths ( $\Gamma$ ,  $\text{cm}^{-1}$ ), and absorption integral coefficients ( $A \cdot 10^8 \text{ cm}^2 \cdot \text{molec}^{-1} \cdot \text{c}^{-1}$ ) of vibrational bands  $^{238}\text{UF}_6$ .

Gas	Solution in LXe		A	Interpretation
	$\nu$	$\Gamma_{\text{exp}}$		
627.2	618.3	1.8±0.2	440	$\nu_3(\text{F}_{1u})$
822.0	816.0	3.0±0.5	0.23	$\nu_3+\nu_5(\text{F}_{1u}+\text{F}_{2u}+\text{A}_{2u}+\text{E}_u)$
1158.1	1144.4	4.7±0.5	0.96	$\nu_2+\nu_3(\text{F}_{1u}+\text{F}_{2u})$
1292.1	1281.0	3.0±0.5	0.76	$\nu_1+\nu_3(\text{F}_{1u})$
1688.5	1671.0	5.0±1.0	0.022	$2\nu_2+\nu_3(\text{F}_{1u}+\text{F}_{2u})$
1823.0	1806.9	4.0±1.0	0.008	$\nu_1+\nu_2+\nu_3(\text{F}_{1u}+\text{F}_{2u})$
1871.5	1849.0	13.0±2.0	0.01	$3\nu_3(2\text{F}_{1u})$

In order to determine the character of the  $\text{UF}_6$  intermolecular interactions in the cryogen solution, we have obtained the correlation dependencies of the  $\text{SF}_6$  and  $\text{UF}_6$  IR-absorption bands halfwidths on the corresponding normalized second moments  $M_2$ . We assumed therewith, that the magnitude of  $c$  is determined only by two broadening mechanisms – vibrational dephasing and rotational diffusion; and, in addition, we neglected the dependence of  $c$  on the vibrational quantum numbers. Under such assumptions, the correlation dependence of  $c$  on  $M_2$  should be linear, because the magnitude of the angular momentum correlation time for all vibrational bands of  $\text{SF}_6$  and  $\text{UF}_6$  is one and the same.

It should be noted, that the corresponding linear dependencies of experimentally observable  $\Gamma$  on the calculated  $M_2$  were conducted through the points

which correspond to transitions into the least split vibrational-rotational states, because in the presence of groups of closely located levels, the character of the dependence may differ from the linear one due to an increase of the vibrational relaxation rate. Besides, for the spherical tops the straight line may be well drawn only through three points:  $\nu_3(F_{1u})$ ,  $\nu_4(F_{1u})$ , and  $\nu_5 + \nu_6(F_{2u})$ , because the bands only of these vibrational-rotational states are not disturbed at the sacrifice of the Coriolis interaction.<sup>9,10</sup>

A comparative analysis of the obtained correlation dependencies has shown, that the amplitude of  $M_2$  variation within the limits  $\nu_3 - (\nu_5 + \nu_6)$  for  $UF_6$  is almost an order of magnitude less than the corresponding value for  $SF_6$ . This fact together with significant difference between the calculated and the experimental values of  $c$  for the  $UF_6$  absorption bands, found earlier,<sup>11</sup> testify that the processes of vibrational dephasing and rotational diffusion significantly contribute into formation of the  $UF_6$  bands contours as opposed to its isoelectron analog  $SF_6$ .

Since the spectroscopic data, obtained from the cryospectra (in contradiction to other methods, for example, matrix isolation), are similar to the data on the gaseous phase,<sup>6</sup> then a uniformity of the mechanisms of the vibrational bands contours formation in  $UF_6$  spectra under atmospheric conditions and in the cryogen solution should be expected.<sup>12</sup>

The data on the parameters of vibrational bands within the  $MoF_6$  and  $WF_6$  IR-spectra in gas phase and in a solution of liquefied Kr are presented in Table II. The data of Table II show an essential difference between the halfwidths of the  $MoF_6$  and  $WF_6$  bands contours. It is mainly attributed to the bands contours' superposition of isotopic modifications of these molecules. An analysis of the correlation dependencies has shown that the amplitude of  $M_2$  variation within the limits  $\nu_3 - (\nu_5 + \nu_6)$  only slightly differs from that for  $UF_6$ . It indicates that the process of vibrational dephasing contributes significantly (as well as in the case of  $UF_6$ ) into formation of the  $MoF_6$  and  $WF_6$  bands contours.

TABLE II. Frequencies ( $\nu$ ,  $cm^{-1}$ ) and halfwidths ( $\Gamma$ ,  $cm^{-1}$ ) of the  $MoF_6$  and  $WF_6$  vibrational bands of natural isotope composition.

MoF <sub>6</sub>			WF <sub>6</sub>			Interpretation
Gas	Solution in LKr		Gas	Solution in LKr		
$\nu$	$\nu$	$\Gamma_{exp}$	$\nu$	$\nu$	$\Gamma_{exp}$	
743.1	735.0	8.0 ± 0.3	713.0	707.2	1.8 ± 0.2	$\nu_3(F_{1u})$
1052.9	1044.5	10.5 ± 0.5	1028.3	1020.7	3.7 ± 0.5	$\nu_3 + \nu_5 (F_{1u} + F_{2u} + A_{2u} + E_u)$
1389.0	1381.6	9.1 ± 0.5	1387.0	1380.4	3.3 ± 0.5	$\nu_2 + \nu_3 (F_{1u} + F_{2u})$
1480.8	1473.1	6.2 ± 0.5	1483.1	1475.6	3.4 ± 0.5	$\nu_1 + \nu_3(F_{1u})$
–	2025.4	12.3 ± 1.0	–	2051.3	6.4 ± 1.0	$2\nu_2 + \nu_3 (F_{1u} + F_{2u})$
–	2122.2	11.5 ± 1.0	–	–	–	$\nu_1 + \nu_2 + \nu_3 (F_{1u} + F_{2u})$
–	2217.5	14.6 ± 2.0	–	2107.3	12.2 ± 2.0	$3\nu_3 (2F_{1u})$

TABLE III. Frequencies ( $\nu$ ,  $cm^{-1}$ ) of the  $MOF_4$  (M = Cr, Mo, W, U) and  $MO_2F_2$  (M = Cr, Mo, U) vibrational bands of natural isotope composition.

Molecule	$\nu_1$	$\nu_2$	$\nu_3$	$\nu_4$	$\nu_5$	$\nu_6$	$\nu_7$	$\nu_8$	$\nu_9$
CrOF <sub>4</sub> *	1026	721	263	631	292	327	778	319	237
WOF <sub>4</sub>	1056	732	249	633	328	290	699	301	231
MoOF <sub>4</sub>	1046	715	262	–	–	–	721	292	236
UOF <sub>4</sub>	891	661	117	559	276	149	646	201	–
CrO <sub>2</sub> F <sub>2</sub> **	1006	727	364	209	259	1017	275	788	305
MoO <sub>2</sub> F <sub>4</sub>	988	692	366	191	–	1009	–	711	274
UO <sub>2</sub> F <sub>2</sub> ***	868	631	146	–	234	1001	–	–	261

\*For molecules  $MOF_4(C_{4v}) \Gamma_{vib} = 3A_1 + 2B_1 + B_2 + 3E$ .

\*\* For molecules  $MO_2F_2(C_{2v}) \Gamma_{vib} = 4A_1 + A_2 + 2B_1 + 2B_2$ .

\*\*\*IR-spectrum for solid specimen was obtained at  $T = 160$  K.

Table III presents the values of the basic vibration frequencies for  $UOF_4$  and  $UO_2F_2$ , and oxifluorides of some metals of the chromium group obtained primarily by methods of high-temperature IR-spectroscopy and matrix isolation. The application of just these

spectroscopic methods is stipulated by the fact that as the temperature increases the oxifluorides of the transient metals evaporate in the form of monomeric molecules, whereas under standard conditions these compounds (except for  $UOF_4$ ) exist in the form of

solid crystal hydrates.<sup>13</sup> According to the mass-spectrometric data,<sup>14</sup> some oxifluorides of these metals polymerize at the pressures  $\geq 1$  Torr. At the same time the results of strain-measuring investigation point to the fact that the majority of oxifluorides of transient metals in gas phase partly decompose and disproportionate.

Note, that a separation of frequencies within vibrational spectra of the oxifluorides from the chromium group of elements is hindered due to significant bands overlapping.<sup>13</sup> So, it is necessary to perform additional calculations for the contours of a series of bands (for example, the bands related to the metal-oxygen bonds, etc.), what prohibits correct estimation of integral absorption coefficients.

The vibrational spectra of the transient metals tetrafluorides (including  $UF_4$ ) are presently obtained only under conditions of these molecules isolation in low-temperature matrices.<sup>13,15</sup> It is connected with the fact that practically all halides of tetravalent metals (as opposite to the oxihalides) are poorly volatile, and at high temperatures evaporate as monomeric tetrahedral molecules of  $T_d$  symmetry. In solid state these compounds exist both in the form of polymers and crystal hydrates.<sup>13</sup> In the vibrational spectrum of matrix-isolated  $UF_4$  molecules two bands with maxima at 597 and 532  $cm^{-1}$  are observable, related, correspondingly, to full-symmetric and antisymmetric valent vibrations  $\nu_1(A_1)$  and  $\nu_3(F_{1u})$  of tetrahedral configuration.

We have to note to our regret, that even in the latest versions of the spectroscopic databases (HITRAN-96, GEISA, etc.) the information on the above-listed radioactive compounds is absent. So, when analyzing the presently available data on the vibrational spectra of the uranium fluorides and oxifluorides from the point of view of their use in remote laser sounding of the radioactive and toxic components of the emergency emissions, a series of factors should be taken into account. Either of the  $UOF_4$  and  $UF_4$  compounds may form two polymorphous modifications. The  $UF_4$  and  $UO_2F_2$  in turn are characterized by their ability to form several crystal hydrates.

A thoroughful analysis of the presently available scanty spectroscopic data, sometimes inconsistent, performed by us, has shown, that the vibrational spectra of the hydrates  $UF_4 \cdot nH_2O$  ( $2.5 \geq n \geq 0.5$ ) and  $UO_2F_2 \cdot nH_2O$  ( $3 \geq n \geq 2$ ) as a part of the aerosols may essentially differ from the spectra of isolated molecules  $UF_4$  and  $UO_2F_2$  and significantly depend on the magnitude of  $n$ . So, the maximum of antisymmetrical vibration band within the spectrum of IR-absorption of the rhombic crystal hydrate  $UF_4 \cdot 2.5H_2O$  (as opposite to the data on matrix-isolated uranium tetrafluoride) is  $\cong 430$   $cm^{-1}$ , cubic crystal hydrate  $UF_4 \cdot 1.9H_2O$  –  $\cong 410$   $cm^{-1}$ , and monoclinic crystal hydrate  $UF_4 \cdot 1.4H_2O$  –  $\cong 405$   $cm^{-1}$ . Besides, the intense bands of the  $H_2O$  vibrations with maxima at  $\cong 1600$  and

$\cong 3400$   $cm^{-1}$  are present within the  $UF_4 \cdot nH_2O$  IR-spectrum, which shift to the longwave spectral range by more than 100  $cm^{-1}$  as  $n$  decreases.

This fact together with these bands broadening to  $\cong 500$ – $700$   $cm^{-1}$  in the case of monoclinic crystal hydrate point to the presence of hydrogenous bonds in the uranium tetrafluoride crystal hydrates. As for uranyl-fluoride  $UO_2F_2 \cdot nH_2O$ , a systematic study of  $n$ -dependencies of the IR-spectra are as yet absent. But the results of X-ray diffraction investigations<sup>16</sup> show that the length of the bonds U–F and U–O in  $UO_2F_2 \cdot nH_2O$  depends on  $n$ . Therefore, by analogy with  $UF_4 \cdot nH_2O$ , one should expect a noticeable longwave shifts of the bands maxima corresponding to the bonds U–F and U–O vibrations.

The molecules of hydrogen fluoride are being formed practically at all stages of interaction of the uranium hexafluoride and the products of its hydrolysis with water vapors, gaseous components of an emergency emission, and the atmospheric gases. Although the parameters of the molecule HF are well known and may be found practically in all spectroscopic databases, their application to the problems of the emergency emission components control would not be entirely appropriate. It is connected with the fact that when the molecules HF interact with the water vapor in the atmosphere, they may form a stable gas-phase complex (hydrate)  $HF \cdot H_2O$ .

The conducted in investigation<sup>17</sup> of IR-spectrum of that complex, using the diffraction spectrophotometer, has shown it to be characterized by three additional absorption bands corresponding to vibrations of intermolecular bond: two of them are in the range of HF and  $H_2O$  vibrations and one – in the range from 780 to 800  $cm^{-1}$ , i.e. in the range of vibration of the complex itself. The performed therewith estimates of the complex formation enthalpy variation gave the value  $-6.2$   $kcal \cdot mol^{-1}$ , which corresponds to the dissociation energy  $-5.5$   $kcal \cdot mol^{-1}$  and total dissociation energy  $-7.1$   $kcal \cdot mol^{-1}$ .

For the most molecular gases the depth of the intermolecular potential well  $D_e$  has the order of the molecules progressive energy at the critical temperature:  $D_e = kT_c$ , where  $T_c$  is the critical temperature. At  $T < T_c$  the energy of the molecules interaction exceeds the thermal one, what, in fact, leads to a formation of the stable gas-phase complexes. Therewith, the quantity of the complexes sharply changes depending on the temperature and the pressure.<sup>18</sup> For equilibrium process of the complex formation, schematically presented as



the equilibrium constant is<sup>19</sup>

$$\frac{n_{X \dots YZ}}{n_X n_{YZ}} = \left( \frac{h^2}{2\pi k T \mu} \right)^{3/2} \exp \frac{D_0}{RT}, \quad (9)$$

where  $n_{X...YZ}$  and  $n_X$ ,  $n_{YZ}$  are the number densities of complex compounds and interacting particles in equilibrium vibrational-rotational state,  $D_0$  is the energy of dissociation, corresponding to this state, and

$$\mu = (M_X M_{YZ}) / (M_X + M_{YZ}), \quad (10)$$

where  $M_i$  is the molar mass.

The equilibrium constant can be determined experimentally by the methods of high resolution IR-spectroscopy and microwave spectroscopy from measurements of the absolute intensities of rotational transitions of the reactions (8) participants in an equilibrium gaseous mixture. With the equilibrium constant obtained in such a way, it is possible to estimate rigorously the magnitude of the dissociation energy  $D_0$  in the ground vibrational-rotational state, connected with the total dissociation energy  $D_e$  by relation<sup>19,20</sup>

$$D_e = D_0 + N_A \sum_i [2h \nu_i (X...YZ)]^{-1} - N_A \times \sum_i [2h \nu_i (X)]^{-1} - N_A \sum_i [2h \nu_i (YZ)]^{-1}, \quad (11)$$

where  $N_A$  is the Avogadro number; under the sum sign there are the contributions from all vibration states except for intermolecular deformation vibrations in the gas-phase complex of  $X \dots YZ$  type.

The conducted investigations<sup>20-22</sup> of the gaseous hydrate HF·H<sub>2</sub>O in the equilibrium phase ( $n(\text{H}_2\text{O}) = 1.85 \cdot 10^{19}$ ,  $n(\text{HF}) = 6.7 \cdot 10^{20}$ ,  $n(\text{HF} \dots \text{H}_2\text{O}) = 0.3 \cdot 10^{14} \text{ m}^{-3}$ ) by the microwave spectroscopy method allowed the authors of these papers to find the value of that complex dissociation energy  $D_0 = -8.1 \text{ kcal} \cdot \text{mol}^{-1}$ . According to (11), the estimates of the total dissociation energy give the value  $D_e = -10.2 \text{ kcal} \cdot \text{mol}^{-1}$ , which agrees well with the results of nonempirical quantumchemical calculations,<sup>23</sup> i.e.  $-9.1 \text{ kcal} \cdot \text{mol}^{-1}$ . It should be noted here, that the latter value is noticeably higher than the value of  $D_e$  obtained from the IR-spectra<sup>17</sup> ( $-7.1 \text{ kcal} \cdot \text{mol}^{-1}$ ) whereas the IR-spectroscopic values of the complex enthalpy slightly differ from the calculated<sup>23</sup> one ( $\Delta H^{298} = -6.2$  and  $-7.0 \text{ kcal} \cdot \text{mol}^{-1}$ ). *Ab initio* calculations of HF·H<sub>2</sub>O structural parameters give the value 0.272 nm for the distance between the hydrogen-bonded atoms F and O, which correlates well with our estimates (0.265 nm) performed under the assumption that the complex's structure is  $\text{FH} \dots \text{O} \begin{matrix} \text{H} \\ \diagdown \\ \text{H} \end{matrix}$  with the angle  $\Theta = 4.5^\circ$  between the hydrogen and F–O bonds.

Aside from the mentioned peculiarities of the HF molecules interaction with water vapor, several additional factors should be considered. Unlike the spectra of pure HF and H<sub>2</sub>O, the rotational structure of the absorption bands HF·H<sub>2</sub>O is expressed weaker and the vibrational frequencies of the H–F and H–O bonds in the hydrate (similarly to the crystal hydrates of the uranium fluorine-containing compounds) are significantly (several tens of  $\text{cm}^{-1}$ ) shifted to the

longwave region. The molecules HF and H<sub>2</sub>O may exist under atmospheric conditions in the form of weakly bonded nonrigid molecular complexes (polymers or dimers)<sup>24-26</sup> characterized by low energy (usually 1–2  $\text{kcal} \cdot \text{mol}^{-1}$ ) of the forming bonds. An interaction of these nonrigid van der Waals complexes results (as well as in the case of monomer molecules HF and H<sub>2</sub>O) in a formation of structurally nonrigid gaseous hydrate with general formula  $(\text{HF})_n \cdot (\text{H}_2\text{O})_m$ , where  $n, m \geq 2$ .

In distinction to the gas-phase complex HF·H<sub>2</sub>O, observed earlier, the nonrigid hydrate  $(\text{HF})_n \cdot (\text{H}_2\text{O})_m$  is characterized by several types of motions of large amplitude, what, in turn, may result in much more noticeable transformation of the vibrational spectrum of this complex and, consequently, in serious methodological difficulties connected with its detection in the atmosphere by means of remote laser sounding facilities.

The analysis of the main stages of NFC, conducted in this work, along with the study of the vibrational spectra of the uranium fluorides and oxifluorides, the elements from the chromium subgroup in various aggregate states, and the characteristics of structurally nonrigid molecular complexes with HF and H<sub>2</sub>O participation allowed us to found a series of spectrochemical peculiarities of these systems under atmospheric conditions.

The obtained results provide a possibility to predict the behavior of the most dangerous radioactive and toxic components of the emergency emissions from the NFC plants, taking into account their participation in different chemical reactions with water vapors, atmospheric gases, organic and inorganic components of the emission, as well as to determine the character of their intra- and intermolecular interactions, and their contribution into transformation of the vibrational spectra of the objects of the remote laser sounding.

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