Dynamics of the UF$_6$ hydrolysis in the atmosphere from the experimental studies of the variations in its IR absorption spectrum

I.I. Zherin, S.T. Penin, and Z.S. Penina

Institute of Atmospheric Optics,
Siberian Branch of the Russian Academy of Sciences, Tomsk

Experimental results of studying the variation of the IR absorption spectrum of UF$_6$ in a band centered at 623 cm^{-1} during the process of UF$_6$ hydrolysis in the atmosphere are presented. The results obtained show that hydrolysis in a volume lasts for a long time, i.e., we can conclude that in the case of UF$_6$ emission to the atmosphere, its free hexafluoride lives in air for a long time. These results confirm the data of indirect measurements on characteristic times of the reaction based on scattering of laser radiation by aerosol particles produced at the hydrolysis.

The need in monitoring of toxic and radioactive emissions to the atmosphere and areas nearby the nuclear-cycle enterprises caused by their strong threat for the environment and human health has stimulated the research into the new methods enabling determination of the chemical and radioactive contaminants content in the atmosphere.

The study of the aerosol formation dynamics based on scattering of laser radiation at hydrolysis of the UF$_6$ under conditions imitating the atmospheric ones[1–4] enabled collecting the data characterizing implicitly the process of hydrolysis itself. In particular, it was found that non-hydrolyzed UF$_6$ remains in the process of active hydrolysis regardless of the concentrations studied and stoichiometric relationships of the initial components.

In the case of low UF$_6$ concentrations, the process of aerosol formation at hydrolysis slows down almost exponentially with the decrease of the concentration, but the levels of forward and backward scattering signals point that there exist a residual UF$_6$ (penetrating fraction) for a long time (at least up to 2 h).

Hydrolysis in a volume with the formation of aerosol fraction proceeds even at ultralow pressure of UF$_6$ (UF$_6$ ~ 10^{-5}–10^{-6} Torr) close to the level of maximum permissible concentration.

These results stimulate application of optical methods to conduct direct studies of the dynamics of UF$_6$ hydrolysis in the atmosphere.

In this paper, we describe an experimental study of the dynamics of UF$_6$ hydrolysis in air by the methods of IR absorption spectroscopy.

The studies of UF$_6$ by the methods of IR absorption spectroscopy have been carried out since the early 1950's. The results of these studies became classical, and the IR absorption spectra of the UF$_6$ have been discussed in many papers and books. The data on the parameters of the IR vibrational absorption bands of gaseous UF$_6$ in natural abundance are tabulated below.

Table 1. Wavenumbers (ν, cm^{-1}) and the integral absorption coefficients ($A \cdot 10^8$ cm$^2 \cdot$mol$^{-1} \cdot$s^{-1}) of the vibrational bands of ^{238}UF$_6$

ν	A	Assignment
623.2	440	$\nu_3(F_{1u})$
822.0	0.23	$\nu_3+\nu_5(F_{1u}+F_{2u}+A_{2u}+E_u)$
1158.1	0.96	$\nu_2+\nu_3(F_{1u}+F_{2u})$
1292.1	0.76	$\nu_1+\nu_3(F_{1u})$
1688.5	0.022	$2\nu_2+\nu_3(F_{1u}+F_{2u})$
1823.0	0.008	$\nu_1+\nu_2+\nu_3(F_{1u}+F_{2u})$
1871.5	0.01	$3\nu_3(2F_{1u})$

The value $A = (440 \pm 60)$ cm$^2 \cdot$mol$^{-1} \cdot$s^{-1} for the band of the antisymmetric stretching vibration $\nu_3(F_{1u})$ agrees well with the data from Ref. 5 obtained from the IR absorption spectra of gaseous UF$_6$ recorded with the use of a diode laser ($\Delta\nu = 10^{-4}$ cm^{-1}) and a multipass cell with $L = 80-400$ m at the UF$_6$ vapor pressure $P = 10^{-1}-10^{-3}$ Torr. The values of A for the bands corresponding to the second-order transitions with the participation of the ν_3 quantum range within $(1-0.2) \cdot 10^{-8}$ cm$^2 \cdot$mol$^{-1} \cdot$s^{-1}, and those for the bands corresponding to the third-order transitions range within $(0.02-0.01) \cdot 10^{-8}$ cm$^2 \cdot$mol$^{-1} \cdot$s^{-1} (Ref. 6).

Regardless of a large number of papers devoted to the IR absorption spectra of UF$_6$, the behavior of the spectrum of free UF$_6$ in air have until so far been only poorly studied. The interfering factor in detecting low concentration of the free UF$_6$ in the atmosphere may be that the UF$_6$ absorption spectrum overlaps with the spectra of the products of its hydrolysis. Table 2 presents the frequencies of the fundamental vibrations of UOF$_4$ and UO$_2$F$_2$ obtained mostly with the use of the technique of high-temperature IR absorption spectroscopy and matrix isolation.[7]

As seen from Table 2, the presence of bands with the frequencies ν_2 for both of the compounds significantly complicates identification of the free UF$_6$ in the process of its hydrolysis in the humid air.

Table 2. Wavenumbers (ν, cm^{-1}) of the vibrational absorption bands of UOF$_4$ and UO$_2$F$_2$ in natural isotopic abundance

Molecule	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9
UOF$_4$	891	661	117	559	276	149	646	201	–
UO$_2$F$_2$*	868	631	146	–	234	1001	–	–	261

* IR absorption spectrum of a solid sample at T = 160 K.
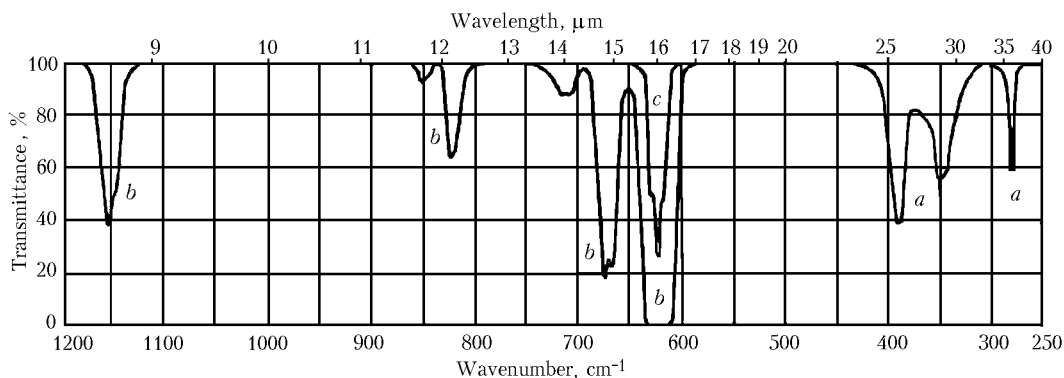
Fig. 1. IR absorption spectrum of UF$_6$: 0.613 atm (*a*), 125 Torr (*b*), and 1 Torr (*c*).

The above-said facts demonstrate the need in further investigations aimed at seeking a possibility of applying the methods of IR absorption spectroscopy to monitoring low content UF$_6$ in the atmosphere.

As was mentioned above, absorption of IR radiation by UF$_6$ molecules is caused by a set of vibrational modes and their combinations. It is seen from Table 1 that the strongest absorption of IR radiation is observed in the band with the central wavenumber ν_3 = 623 cm^{-1}. In this band, the integral absorption coefficient is at least 1000 times higher than those in other bands and equals to $440 \cdot 10^8$ cm$^2 \cdot$mol$^{-1} \cdot$cm^{-1}. Figure 1 depicts the absorption spectrum of gaseous UF$_6$ in the IR region borrowed from Ref. 8, which has already become a classical paper. It is obvious that only measurements in the absorption band centered at ν_3 = 623 cm^{-1} can be productive at low concentrations of the UF$_6$.

It is just for this reason that all our measurements have conducted in this spectral region.

Experimental technique

Absorption spectra of UF$_6$ were recorded with a commercial IKS-29 spectrophotometer using a dual-beam optical arrangement. A reactor cell of stainless steel with polished inner walls and AgCl windows was placed in one arm of the spectrophotometer. The same, but evacuated cell, or a compensator compensating for the absorption by the windows of the measurement cell was placed in the other arm. Experiments were conducted in two stages. At the first stage, the pre-evacuated reactor cell was filled with UF$_6$ at a pressure of 10 to 0.1 Torr, and the UF$_6$ absorption spectrum was recorded in the region of 650–600 cm^{-1}. The above pressure range corresponds to the mass concentration of UF$_6$ (at the temperature of 23°C) from 190 to 1.9 g·m^{-3}. At the second stage, the experiment on direct measurements of the UF$_6$ absorption in the process of hydrolysis at atmospheric pressure was conducted for the first time. In this experiment, the spectrophotometer was tuned at the wavenumber of maximum absorption (623 cm^{-1}), and then the cell was filled with UF$_6$ at a pressure of 1.9 and 1 Torr (mass concentration of 36.1 and 19 g·m^{-3}, respectively). Then the reactor cell was filled with the atmospheric air, the absorption spectrum at 623 cm^{-1} was recorded, and the following parameters were measured: variation of absorption with time, temperature of the ambient medium, and relative humidity of the air (consequently, concentration of H$_2$O molecules in the reactor cell). This technique allows a comparison of the data of implicit measurements[1–4] with the data of direct measurements to be performed.

Results and discussion

Figure 2 depicts the UF$_6$ absorption spectra at different pressures. It should be noted that here we consider absorption of IR radiation (that is, curves in Fig. 2 are mirror-reflected with respect to the plot in Fig. 1). One can see how strongly the absorption varies depending on the UF$_6$ pressure.

It is worth noting the presence of a wide absorption band in the region of 628–640 cm^{-1}. The nature of this band is still unclear. We can only see that the absorption in this band tends to saturation with the increasing UF$_6$ pressure. It is quite possible that the appearance of this band is connected with the UO$_2$F$_2$ particles generated on the inner glass surface at high concentration of UF$_6$ due to its interaction with the moisture on the cell windows. This assumption is based on the existence of the UF$_6$ absorption band with the mode of ν_2 = 631 cm^{-1} (see Table 2). Figure 3 borrowed from Ref. 9 depicts the spectrum of UO$_2$F$_2$. We can see quite a strong absorption in the region of 630–650 cm^{-1}. This band is most probably absent in

free air. This problem, to be finally solved, calls for further investigations. However, even in the presence of the interfering band, we can see that the UF$_6$ band at 623 cm^{-1} is well resolved. Using the data from Fig. 2, we have plotted the dependence of the absorption on the UF$_6$ pressure (Fig. 4). The experimental curve was smoothened using a third-order polynomial. The coefficients were fitted through successive iterations to achieve the closest agreement. As is seen from the plot, the Bouguer$-$Lambert law is partially violated, what is also likely connected with the presence of an absorbing layer at the cell windows.
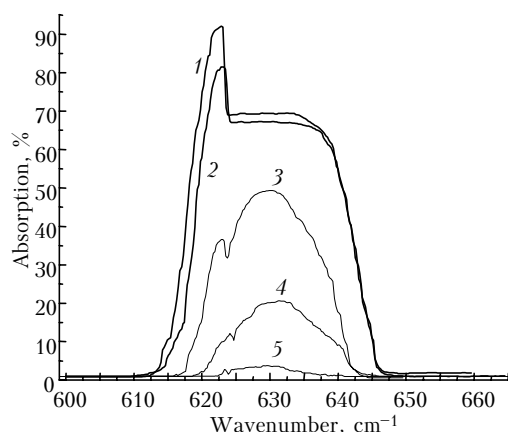

Fig. 2. IR absorption spectrum of UF$_6$ in the region of 600$-$670 cm^{-1} at different pressures: 6.1 (curve *1*), 4.1 (*2*), 1.0 (*3*), 0.4 (*4*), and 0.25 Torr (*5*).

Let us consider now the results of the second stage of our study, namely, direct measurements of the absorption in the band centered at 623 cm^{-1} in the process of UF$_6$ hydrolysis in atmospheric air. As was

already mentioned above, the spectrophotometer scale in these measurements was set at the center of the absorption band, the cell was filled with UF$_6$, and then recording of the spectrum was started. Then a valve was opened, and atmospheric air came into the cell. As a result, we measured the variation of the absorption and, consequently, the variation of UF$_6$ concentration in time. Hydrolysis was studied at two values of the initial UF$_6$ pressure: 1 and 1.9 Torr (mass concentration of 19 and 36.1 g·m^{-3}, respectively).

In both experiments, the temperature of the ambient air was 23°C at the relative humidity $\sim$ 80%. Under such conditions, the partial pressure of water vapor in air was $\sim$ 17 Torr. Consequently, the stoichiometry conditions were certainly fulfilled. However, for the UF$_6$ pressure of 1.9 Torr the condition of tenfold excess of the concentration of water molecules was broken. The experimental results are depicted in Figs. 5 and 6.

Although the experimental data are still under processing, some interesting conclusions can be drawn already now. In both of the experiments, we have observed, once the valve has been opened, a sharp decrease in the absorption (during the first 40$-$50 s), in spite of the fact that the pressure in the cell became equal to the atmospheric pressure, i.e., the background absorption increased.

It is seen from Fig. 5 that the pressure decreases considerably for 35$-$38 min, then the curve becomes smoother and agrees well with the polynomial. These results are in a close agreement with the data on light scattering. The same can be seen from analysis of Fig. 6. In this case, the decrease (but smoother than in the first case) is observed in the first 30 min after the beginning of the hydrolysis.
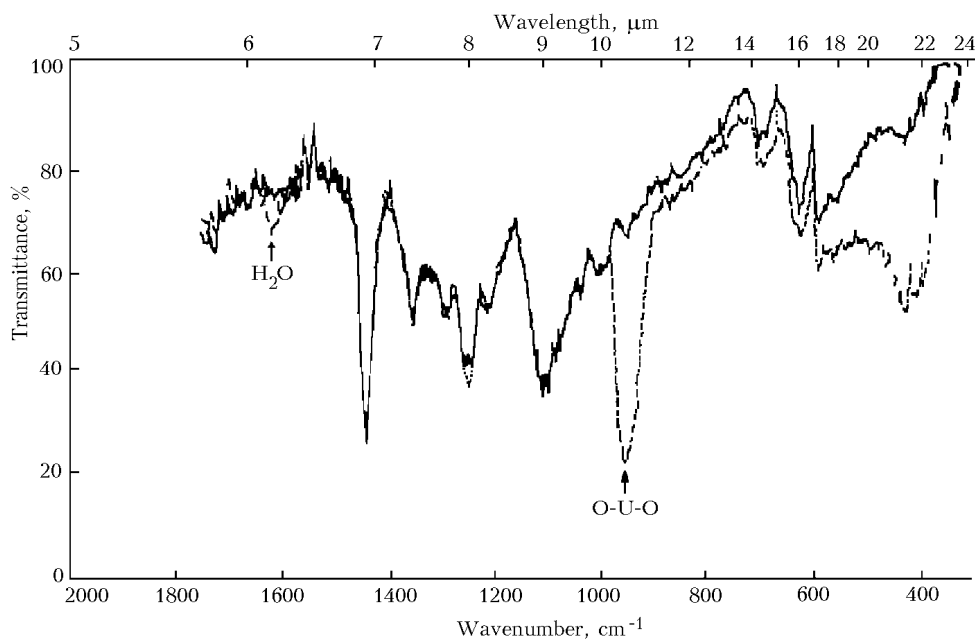

Fig. 3. Absorption spectrum of UO$_2$F$_2$: aerosol particles (dashed curve) and on a filter (solid curve).

This is quite explainable, if we take into account that in this case there is no tenfold excess of the concentration of water molecule over the concentration of the UF_6 one and this coincides with the earlier results on scattering.
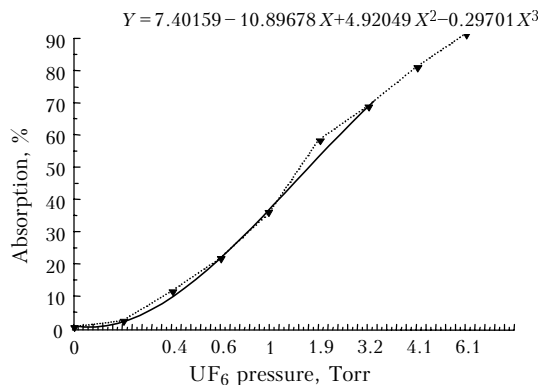
$$Y = 7.40159 - 10.89678\,X + 4.92049\,X^2 - 0.29701\,X^3$$

Fig. 4. Pressure dependence of the UF_6 absorption: experiment (dashed curve) and polynomial approximation (solid curve); the polynomial equation is given in the figure.
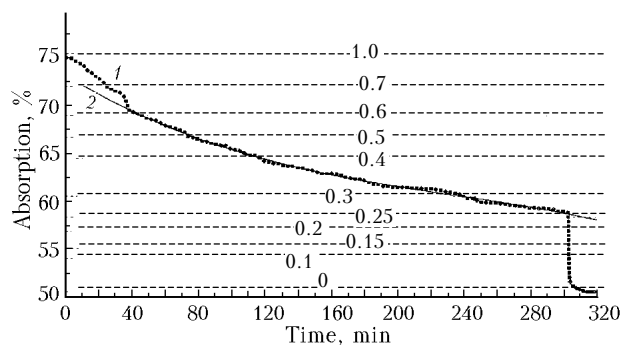
Fig. 5. Variation of UF_6 pressure with time at hydrolysis in atmospheric air at the initial pressure of 1 Torr: experimental data (curve *1*), smoothing by a polynomial (*2*); the numbers on dashed straight lines show the UF_6 partial pressure corresponding to the given value of the absorption.
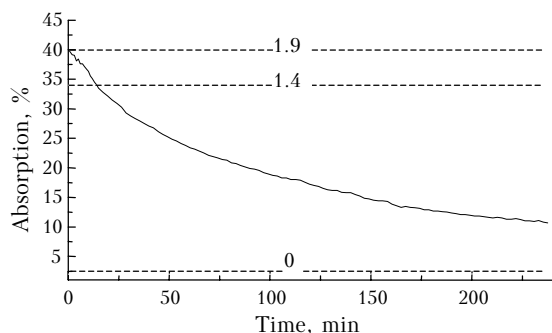
Fig. 6. Variation of the absorption with time at UF_6 hydrolysis in the atmosphere; 1.9, 1.4, and 0 are the values of the UF_6 pressure and the dashed straight lines show the corresponding values of the absorption (initial pressure of 1.9 Torr).

For us the fact that hydrolysis continued even after 5 h, i.e., the curve did not achieve the zero level (sharp decrease of the absorption after 300 min in

Fig. 5 is caused by evacuation of the cell, which started just at that time) seems to be most interesting. That slow reaction may be caused by the fact that hydrolysis proceeded in a closed volume without active mixing. Besides, some error in measurements could be caused by UF_6 particles deposited on the cell windows. This could introduce an error into the rate of decrease of the curve describing the value of the absorption and, consequently, cause underestimation of the final concentration of the UF_6. However, the fact that the curve still continued to decrease and, consequently, the concentration of UF_6 in the cell decreased as well evidences that hydrolysis in the cell continued all the time.

Based on the above-said, we can draw the following conclusions.

The presence of a strong absorption band centered at 623 cm^{-1} and not overlapped by absorption bands of the major atmospheric gases in the spectrum of UF_6 allows the methods of IR spectroscopy to be used for detection of UF_6 in the air.

The spectrum of UF_6 is well resolved and can be separated with the use of commercial spectrophotometers for medium concentrations of the UF_6.

The experiments on direct measurements of the dynamics of UF_6 hydrolysis at atmospheric pressure support the data of indirect measurements of characteristic reaction time from scattering of laser radiation. Consequently, free UF_6 keeps in air for a long time after UF_6 emission.

In conclusion, we would like to say that to study the process of hydrolysis of ultralow concentrations of UF_6 in air, it is useful to improve the selectivity of excitation of the vibrational mode and to increase the pump energy. For this purpose, laser sources can be used (there are commercial diode lasers with the wavelength of 16 µm), and this could allow the sensitivity of the method to be increased.

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