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FLUORINE ABSORPTION SPECTRA AND SOME FLUORIDES IN CONDENSED STATE

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SUMMARY

The absorption spectra of liquid F_2, NF_3, N_2F_4, CF_4, BF_3, NF_3, SF_6 have been obtained at diminished temperatures in the near ultra-violet region of the spectrum. It is shown that the absorption spectrum does not differ from the spectra in the gaseous phase, therefore the elementary absorption act is characterized by the cross section of photon absorption by an individual molecule. The absorption cross sections of the above mentioned molecules are represented in the liquid phase, which do not differ strongly from absorption cross sections of these molecules in the gaseous phase. The dependence of the absorption cross sections of liquid fluorine on its concentrations in solutions with N_2, Ar, NF_3, O_2 at - 196°C has been studied. The cross sections of photon absorption by the fluoride molecule in different liquid media with small fluorine concentrations have been obtained.

INTRODUCTION

Photochemical processes with participation and formation of inorganic fluorides [1] demands some information about the absorption spectra of these substances. Many reactions involving inorganic fluorides proceed efficiently only at low temperatures when these substances are in liquid state. Therefore investigation of photo absorption of these substances in liquid state is required. This paper is devoted to measurements of the absorption parameters of liquid fluorine and some fluorides as well as liquid mixtures of fluorine with different substances, where the fluorine molecules are the particles absorbing the radiation.

EXPERIMENTAL PROCEDURE

The measurements were carried out in the cell, fabricated taking into account high corrosion activity and toxicity of fluorine and its compounds. The working temperature range was from -196°C to +100°C, the accuracy of thermostativity was ±0,05°. Dispersion of the spectrophotometer was 10 Å/mm and photometric accuracy was 1%. The purity of the substance was checked by mass-spectrometric analyses, fluorine purity was checked by spectrometric analyses, according to the known value of the absorption coefficient in the gaseous phase [2]. Fluorine concentration was determined similarly in its mixtures with argon, oxygen, nitrogen and NF_3.

The optical thickness of the liquid was measured with an accuracy of 0,02 mm. The density of liquid fluorine is 41,0 mole/l [3] at - 196°C, that of liquid NF_3 is 25,8 mole/l [4] at - 196°C, that of liquid CF_4 is 18,7 mole/l [4] at - 130°C.

The density of liquid N_2F_4 was determined according to the equation given in [5] and was 14,8 mole/l at - 97°C. Measurements with liquid SF_6 were conducted at - 49°C and 2.5 atm, and with liquid BF_3 - at - 101°C and 1 atm.

RESULTS AND DISCUSSION

The typical measurement data are given in Figs. 1,2 and in Tables 1,2,3,5. The error in the absorption cross sections was determined as the square mean root value of the experimental errors. A continuous absorption increasing in the short-wave part of the spectrum was observed in all cases. In the visible and near infrared regions of the spectrum (up to 25000Å) the substances investigated are transparent in the condensed phase, and for SF_6 and BF_3, no distinct absorption is observed within the whole wave length range investigated. In the transition to the condensed phase the optical density of the medium increases substantially but the values of the absorption cross sections change only slightly. For example, for NF_3, the absorption band shifts slightly to the short-wave side, and for N_2F_4, the cross sections in the gaseous and condensed phases coincide within the range of measurement errors (see [6] and Tables 2,3). It should be noted that the absorption peak, due to the radical NF_2 in the absorption spectrum of N_2F_4 that is seen clearly in the gaseous phase [6,7] at λ =2600 Å, is lacking in the spectrum of liquid N_2F_4, i.e. the degree of dissociation decreases substantially with decreasing temperature.

Absorption of light radiation in the liquid medium is possible due to formation of different complexes. This may lead to appearance of resonances and bands in the spectrum of liquids, which are lacking or rather weakly pronounced in the gaseous phase. For example, resonances appear in the absorption spectrum of liquid oxygen [8] showing formation of the $(O_2)_2$ complexes (they are clearly seen in Fig.1 for fluorine and oxygen mixtures).

Comparing the data obtained in our work with the results obtained in [6],one can easily see that such effects are not observed in the spectra of liquid fluorine, liquid N_2F_4 and CF_4, and the absorption spectra of these substances in liquid and gaseous states do not differ principally from each other.

At the same time the absorption cross section of the fluorine molecule depends on the type of the particles surrounding it. Fig.2 shows dependence of the cross section of the photon absorption by the fluorine molecule in the binary liquid mixture. It is seen that within the experimental error range each dependence is approximated as a straight line:

$$\sigma = C\,\sigma_{F_2-F_2} + (1-C)\,\sigma_{F_2-A} \quad (1)$$

Here $\sigma_{F_2-F_2}$ and σ_{F_2-A} are the absorption cross section of the fluorine molecule which is in the binary medium consisting of the fluorine molecules with concentration C and type - A molecule or atoms with concentration (1-C), respectively. Generally speaking, the above dependence is not a strict one and corresponds to the assumption that the interaction of the fluorine molecules does not depend on the presence of the type -A particles. Nevertheless this dependence describes reasonably well the results obtained.

TABLE I

The absorption cross-section of liquid F_2 (temperature - 196°C, density 41 mol ℓ^{-1}).

λ, Å	Optical thickness 3,52 mm		Optical thickness 5.25 mm	
	σ, 10^{-2} × ℓ mol.$^{-1}$ cm^{-1}	Relative error,%	σ, 10^{-2} × ℓ mol^{-1} cm^{-1}	Relative error, %
4300	10.8	10	-	-
4400	7.75	6	8.9	23
4500	6.01	5	6.13	9
4600	4.72	5	4.73	5
4800	3.00	5	3.01	5
4900	2.37	6	2.38	5
5000	1.85	7	1.86	5
5100	1.46	8	1.47	5
5200	1.10	10	1.13	6
5300	0.85	12	0.87	7
5400	0.62	16	0.68	8
5500	0.48	20	0.49	11
5600	0.40	27	0.38	13
5700	-	-	0,29	17
5800	-	-	0.21	23

TABLE 2

The absorption cross-sections of liquid NF_3 (temperature -196°C, density 25.8 mol ℓ^{-1}, optical thickness 5.25 mm)

λ, Å	σ, $10^{-2} \times \ell$ mol $^{-1}$ cm^{-1}	Relative error, %
2275	11	14
2300	8.88	9
2325	6.57	6
2350	5.03	5
2375	3.60	5
2400	2.53	5
2425	1.65	7
2450	1.07	9
2475	0.60	14
2500	0.26	25

TABLE 3

The absorption cross-sections of liquid N_2F_4 (temperature - 97°C, density 14.8 mol ℓ^{-1}, optical thickness 2.39mm)

λ, Å	σ, $10^{-2} \times \ell$ mol $^{-1}$ cm^{-1}	Relative error, %
2400	30.1	8
2450	11.2	5
2500	5.0	8
2550	3.1	12
2600	2.0	18
2650	1.6	21
2700	1.3	26
2750	1.2	28

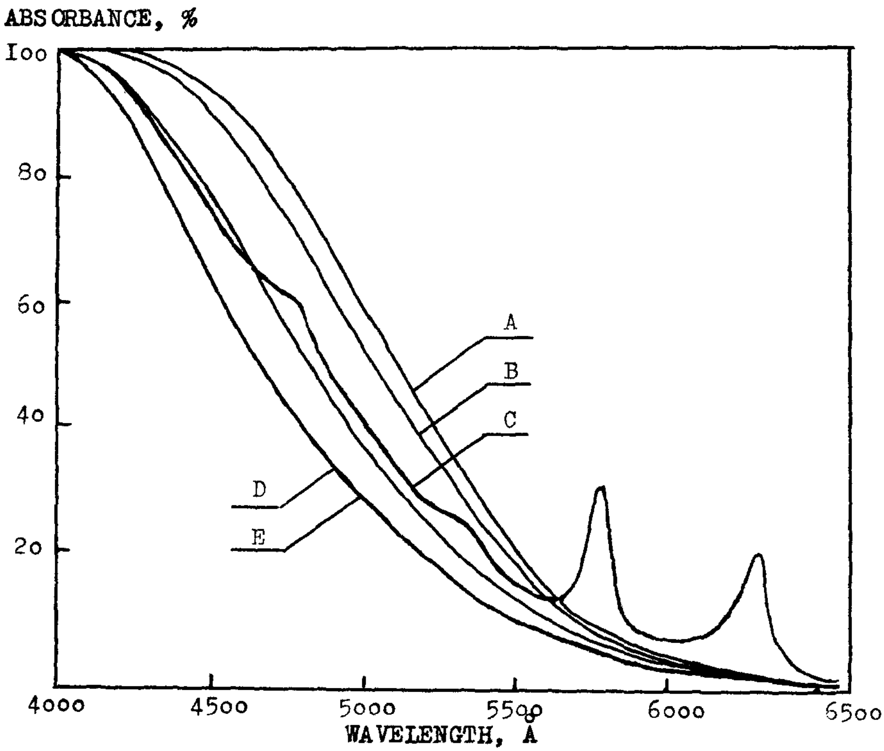

Fig.1. Liquid fluorine absorption spectra and its mixtures at - 196°C and optical thickness 5,25 mm. Trace A: F_2 (concentration of fluorine 99%); Trace B: mixture F_2-Ar (81%); Trace C: mixture F_2-O_2 (38%); Trace D: mixture F_2-NF_3 (53%); Trace E: mixture F_2-N_2 (44%).

The absorption cross sections of the fluorine molecule in different one-component systems with a fluorine concentration tending to zero, may be presented as the work result. Then the absorption cross section in the binary system can be found according to formula (1). The absorption cross sections of the fluorine molecule in liquid fluorine, argon, nitrogen, oxygen and in nitrogen trifluoride with different wave lengths are listed in Table 4.

Apart from the experimental errors a discrepancy in the cross sections is connected with the error arisen in the transition to the limit in the binary medium when the fluorine con-

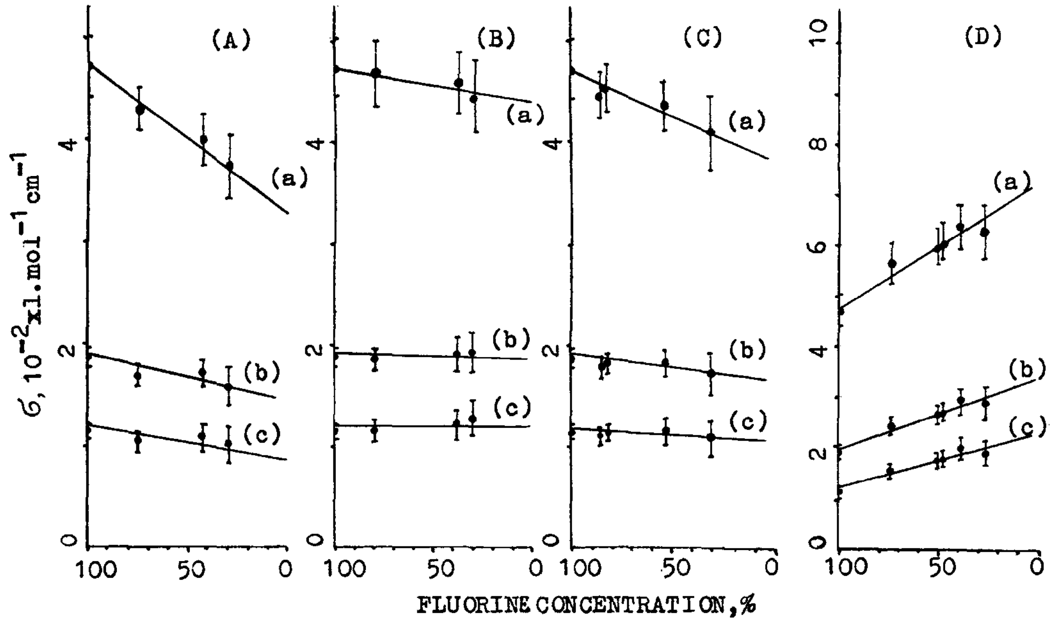

Fig.2. Dependence of liquid fluorine absorption cross-section on solvent concentration at different wavelengthes. (A) System F_2-N_2; (B) System F_2-Ar; (C) System F_2-NF_3; (D) System F_2-O_2. Trace (a): λ =4600Å; Trace (b): λ =5000Å; Trace (c): λ =5200Å.

TABLE 4

Fluorine absorption cross-section at its concentration in the solvent tending to zero

Solvent	λ = 4600 Å		λ = 5000Å		λ = 5200Å	
	$\sigma, 10^{-2}$ $\times \ell\ mol^{-1}\ cm^{-1}$	Relative error, %	$\sigma, 10^{-2}$ $\times \ell\ mol^{-1}\ cm^{-1}$	Relative error, %	$\sigma, 10^{-2}$ $\times \ell\ mol^{-1}\ cm^{-1}$	Relative error, %
O_2	7.1	10	3.3	9	2.3	10
N_2	3.3	20	1.5	20	1.0	28
Ar	4.4	15	1.9	17	1.3	19
NF_3	3.8	17	1.7	17	1.2	11

TABLE 5

Liquid CF_4 absorption cross-section (temperature - 196°C density 18.7 mol/l, optical thickness 10.58 mm)

Å	,10^{-2} x ℓ mol $^{-1}$ cm^{-1}	Relative error, %
2100	1.34	8
2150	1.29	7
2200	1.20	7
2250	1.05	7
2300	0.85	8
2350	0.68	10
2400	0.52	12
2450	0.40	15
2500	0.29	19
2550	0.21	25
2600	0.16	36

centration tends to zero. Taking into account the data of the present work we can draw a conclusion that for the compounds investigated the measurement of the small absorption cross-sections in the long wave region can be performed in the condensed phase using a method simpler than that for the gaseous phase. On the other hand, the high optical density of liquid fluorine allows to conduct photochemical reactions using the long-wave irradiation. The fluorine dissociation energy is 1,6 ev [9] therefore for activation of the process the visible irradiation can be used, which permits to generate the atomic fluorine with various degrees of excitation.

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