

# Isotope Effect in Photoreduction of $^{18}\text{O}$ -Enriched $\text{UO}_2\text{F}_2$ in an Isopropanol Solution

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Received May 25, 2005

**Abstract**—The behavior of the  $[\text{}^{16}\text{O-U-}^{16}\text{O}]^{2+}$ ,  $[\text{}^{16}\text{O-U-}^{18}\text{O}]^{2+}$ , and  $[\text{}^{18}\text{O-U-}^{18}\text{O}]^{2+}$  isotopic species in uranyl fluoride complexes was studied in isopropanol under pulsed UV irradiation of solutions at  $\lambda = 300\text{--}400$  nm. Illumination of the solutions affects the isotope composition of oxygen in uranyl owing to photoreduction and isotope exchange with the water molecules occurring in the solution. The absorption spectra of the  $\text{UO}_2\text{F}_2$  solutions with different isotope compositions of oxygen were measured. The enrichment of  $\text{UO}_2\text{F}_2$  in  $^{18}\text{O}$  only slightly affects the absorption in solution. The IR spectra show that the content of the  $[\text{}^{16}\text{O-U-}^{18}\text{O}]^{2+}$  species in solution decreases more rapidly than that of  $[\text{}^{18}\text{O-U-}^{18}\text{O}]^{2+}$ . Comparison of the photoreduction rates for  $\text{UO}_2\text{F}_2$  species with different isotope compositions of oxygen suggests that this effect cannot be attributed to the difference in the quantum efficiencies of photoreduction for different isotopic species. Accelerated decrease in the content of the  $[\text{}^{16}\text{O-U-}^{18}\text{O}]^{2+}$  species in solution under irradiation was attributed to the excitation exchange processes in uranyl fluoride polymers.

PACS numbers: 82.50.Hp, 82.20.Tr

DOI: 10.1134/S1066362206040072

In this study we examined the behavior of the  $[\text{}^{16}\text{O-U-}^{16}\text{O}]^{2+}$ ,  $[\text{}^{16}\text{O-U-}^{18}\text{O}]^{2+}$ , and  $[\text{}^{18}\text{O-U-}^{18}\text{O}]^{2+}$  isotopic species of uranyl fluoride in isopropanol under UV irradiation of solutions at  $\lambda = 300\text{--}400$  nm. Reactions of photoexcited uranyl with alcohols were the subject of much study, and reactions with molecules of various alcohols were studied in sufficient detail [1–3]. This makes a reaction of this type suitable for studying possible manifestations of isotopy in photochemical reactions of uranyl.

The choice of isopropanol as the reducing agent was governed by its capability to form, in contrast to methanol and ethanol, solvates with  $\text{UO}_2\text{F}_2$  [4, 5]. The occurrence of an isopropanol molecule in the first coordination sphere facilitates reduction of the excited uranyl ion. The spectral region that we selected for excitation of the uranyl complexes is noticeably distant from the absorption spectrum edge, which allows elucidation of the possible role played in the photoreduction by vibronic relaxation involving vibrations of uranyl.

## EXPERIMENTAL

The solutions were irradiated in a mirror elliptic illuminator with an IFP-800 pulse xenon lamp, using

UFS-6 or UFS-8 UV glass filters for cutting out the desired spectral range (300–400 nm). The pulse length was  $\sim 1$  ms, and the interpulse time,  $\sim 10$  s. The solution to be irradiated was placed into an optical quartz test tube with an inner diameter of 9 mm. The test tube was temperature-controlled with distilled water from a thermostat, circulating through a water jacket. Each flash generated  $\sim 10^{17}$  quanta in the test tube containing 4 ml of the solution. The light flux was measured on a Parker actinometer [6].

In all the experiments the test tubes with solutions were kept at a constant temperature of  $20^\circ\text{C}$ . Dissolved oxygen was removed by helium bubbling.

The composition of the solutions was as follows: isopropanol 19, water 0.9, HF 0.1 ml. Keeping the liquid phase of this composition over solid  $\text{UO}_2\text{F}_2$  at room temperature for several days yielded a  $\text{UO}_2\text{F}_2$  solution containing  $\sim 360$   $\mu\text{g ml}^{-1}$  of U. The content of  $\text{UO}_2\text{F}_2$  in the solution can be increased by introducing into isopropanol  $\text{UO}_2\text{F}_2$  dissolved in an  $\text{H}_2\text{O}$ –HF mixture. This yields supersaturated solutions of  $\text{UO}_2\text{F}_2$  which are stable for several days, whereupon precipitation of  $\text{UO}_2\text{F}_2$  becomes noticeable.

$^{18}\text{O}$ -Enriched uranyl fluoride was prepared by the reaction of  $\text{UF}_6$  with an excess of  $\text{H}_2\text{O}$  enriched in  $^{18}\text{O}$ . Both substances were vacuum-distilled in succes-

sion into a Teflon test tube cooled with liquid nitrogen, whereupon the test tube was slowly warmed up to room temperature. The formed HF and excess water were vacuum-distilled from  $\text{UO}_2\text{F}_2$ .

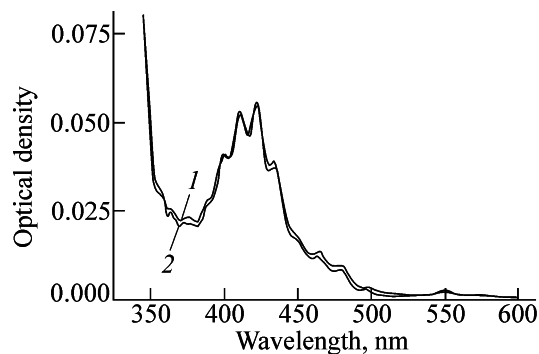
The resulting  $\text{UO}_2\text{F}_2$  preparations contained 42 or 38%  $^{18}\text{O}$ . Neglecting the minor amount of  $^{17}\text{O}$  contained in water, the  $^{18}\text{O}$  distribution in  $\text{UO}_2\text{F}_2$  can be considered as random.

The absorption spectra were measured on a UV-3101 PC Shimadzu spectrometer, and IR spectra, on an FTIR-8700 Shimadzu spectrometer.

During the experiments we determined the UV-induced change in the content of various isotopic species of uranyl in solution and the amount of the resulting  $\text{UF}_4$ . The yield of  $\text{UF}_4$  was estimated from the difference in the U(VI) concentrations in solution before and after the irradiation. The irradiated solution was kept in the dark for 1 day, whereupon the precipitated  $\text{UF}_4$  was separated from the solution by centrifugation. Uranium in solution was analyzed photochemically with Arsenazo III [7].

The proportions of the uranyl groups containing one or two  $^{18}\text{O}$  atoms were determined from the area of the bands in the IR spectra corresponding to anti-symmetric stretching vibrations ( $\nu_{\text{as}}$ ) of the corresponding isotopic species of uranyl converted to  $\text{NaUO}_2(\text{CH}_3\text{COO})_3$  and pressed into a KBr pellet [8]. The method for determining the band areas differed from that used in [8]. The band area  $S_i$  was determined by channel-by-channel summation of the optical densities within the band of interest. The optical density was measured accurately to within 0.001. The background whose nature differed from that of the band of interest was extrapolated by a smooth curve connecting the optical densities beyond the band and was subtracted from the resulting sum. The inaccuracy of determining the band area was estimated at 1–2% from the scatter for several curves extrapolating the background.

To test the applicability of this procedure, we measured the proportions of all the three isotopic species of uranyl upon irradiation of the solution with 45 flashes of the pulse lamp. Channel-by-channel summation of the intensities within each band was carried out with a step of  $0.96\text{ cm}^{-1}$ . The change in the proportion of each isotopic species of  $\text{UO}_2^{2+}$  in solution upon irradiation was taken equal to that in the area of the corresponding band in the IR spectrum of  $\text{UO}_2^{2+}$  isolated from the solution in the form of  $\text{NaUO}_2(\text{CH}_3\text{COO})_3$ . Summation of the proportions of the isotopic species in solution before and after ir-



**Fig. 1.** Absorption spectra of the solutions in isopropanol of  $\text{UO}_2\text{F}_2$  differing in the isotope composition of oxygen. Content of  $^{18}\text{O}$  in uranyl: (1) natural isotope composition and (2) 42%. Uranium concentration in solutions,  $\mu\text{g ml}^{-1}$ : (1) 762 and (2) 753.

radiation showed that, if we take their sum in the initial solution equal to unity, it will be 1.03 in the solution after irradiation, i.e., the divergence is no greater than 3%.

## RESULTS AND DISCUSSION

Introduction of  $^{18}\text{O}$  into the uranyl group affects the extinction of the solutions only slightly. The spectrum exhibits noticeable isotope shifts only for several bands in the vibrational structure of the electronic transitions, corresponding to the stretching vibrations of the uranyl group. These shifts do not exceed 1 nm. Figure 1 shows the spectra.

Table 1 presents the changes in the concentrations of the uranyl enriched in 42%  $^{18}\text{O}$  and uranyl with the natural isotope composition of oxygen in relation to the exposure time of the solution.

The IR spectra in Figs. 2 and 3 illustrate the irradiation-induced changes in the ratio of the isotopic species of uranyl. The UV-induced (45 flashes) changes in the concentrations ( $\mu\text{g ml}^{-1}$ ) of the isotopic

**Table 1.** Changes in the concentration of U(VI),  $\mu\text{g ml}^{-1}$ , in isopropanol solutions of  $\text{UO}_2\text{F}_2$  in relation to the exposure time

Number of flashes	$\text{UO}_2\text{F}_2$ (42% $^{18}\text{O}$ )	$\text{UO}_2\text{F}_2$ , no $^{18}\text{O}$ enrichment
0	635.7	754.9
15	617.4	693.2
30	551.4	650.9
45	531.9	581.5
60	468.2	—

**Table 2.** Areas  $S_i^*$  of the bands of the stretching vibrations  $\nu_{as}$  of  $\text{UO}_2^{2+}$  in the IR spectrum of the isotopic species of  $\text{NaUO}_2(\text{CH}_3\text{COO})_3$  obtained from isopropanol solutions of  $\text{UO}_2\text{F}_2$  before and after irradiation

Experiment no.	$^{18}\text{O}$ content, %	$S_1$	$S_2$	$S_1$	$S_2$
		before irradiation		after irradiation	
1	42	$2.67 \pm 0.02$	$1.22 \pm 0.02$	$1.38 \pm 0.02$	$0.76 \pm 0.02$
2**	17	$0.63 \pm 0.02$	$0.31 \pm 0.02$	$0.24 \pm 0.02$	$0.16 \pm 0.02$
3	42	$2.21 \pm 0.02$	$1.01 \pm 0.02$	$1.74 \pm 0.02$	$0.97 \pm 0.02$
4	38	$4.15 \pm 0.02$	$1.64 \pm 0.02$	$1.65 \pm 0.02$	$0.71 \pm 0.02$
5	38	$4.15 \pm 0.02$	$1.64 \pm 0.02$	$1.86 \pm 0.02$	$0.76 \pm 0.02$
6	38	$4.15 \pm 0.02$	$1.64 \pm 0.02$	$0.65 \pm 0.02$	$0.27 \pm 0.02$
7	38	$4.15 \pm 0.02$	$1.64 \pm 0.02$	$2.26 \pm 0.02$	$0.96 \pm 0.02$
8	38	$4.15 \pm 0.02$	$1.64 \pm 0.02$	$2.56 \pm 0.02$	$1.08 \pm 0.02$

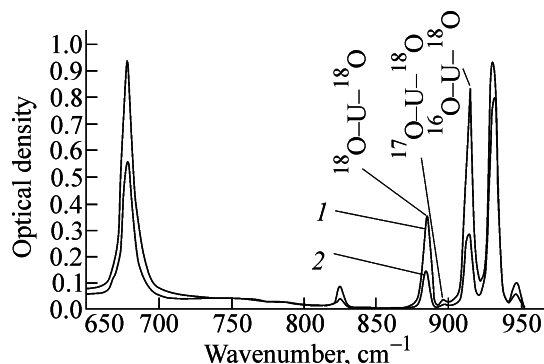
\* Here and hereinafter,  $S_1$  and  $S_2$  refer to the  $[\text{}^{16}\text{O-U-}^{18}\text{O}]^{2+}$  and  $[\text{}^{18}\text{O-U-}^{18}\text{O}]^{2+}$  species, respectively.

\*\* The ratio of  $\text{UO}_2\text{F}_2$  isotopic species is nonrandom.

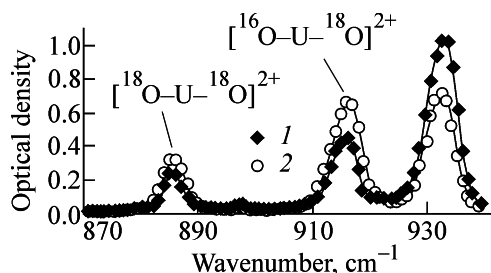
species of uranyl in solution are presented below (the total concentration was determined spectrophotometrically with Arsenazo III, and the concentrations of individual isotopic species, from the IR spectra;

see experiment no. 3 in Table 2).

$\Sigma \text{UO}_2^{2+}$	$[\text{}^{16}\text{O-U-}^{16}\text{O}]^{2+}$	$[\text{}^{16}\text{O-U-}^{18}\text{O}]^{2+}$	$[\text{}^{18}\text{O-U-}^{18}\text{O}]^{2+}$
	Before irradiation		
$635.7 \pm 0.5$	$214 \pm 2$	$310 \pm 3$	$112 \pm 1$
	After irradiation		
$531.9 \pm 0.5$	$251 \pm 2$	$195 \pm 2$	$86 \pm 1$



**Fig. 2.** IR spectrum of  $\text{NaUO}_2(\text{CH}_3\text{COO})_3$  obtained from isopropanol solution of  $\text{UO}_2\text{F}_2$  in the region of the stretching vibrations  $\nu_{as}$  of  $\text{UO}_2^{2+}$  and O-C-O bending vibration  $\delta$  of the acetate group coordinated to the uranyl ion. Initial content of  $^{18}\text{O}$  in  $\text{UO}_2\text{F}_2$  42%. (1) Before and (2) after irradiation.



**Fig. 3.** IR spectrum of  $\text{NaUO}_2(\text{CH}_3\text{COO})_3$  obtained from isopropanol solution of  $\text{UO}_2\text{F}_2$  in the region of the stretching vibrations  $\nu_{as}$  of  $\text{UO}_2^{2+}$  at 38%  $^{18}\text{O}$  content in  $\text{UO}_2^{2+}$ . (1) Before and (2) after irradiation of the  $\text{UO}_2\text{F}_2$  solution.

Table 2 presents the results of treatment of the IR spectra of the  $\text{NaUO}_2(\text{CH}_3\text{COO})_3$  samples obtained before and after UV irradiation from the  $\text{UO}_2\text{F}_2$  solutions of different concentrations, differing in the enrichment in  $^{18}\text{O}$ . In various experiments the solutions were UV-irradiated with 30–80 flashes from the pulse lamp. The optical density in the IR spectra for the first three experiments was measured with a step of  $1.94 \text{ cm}^{-1}$ . Thus, within the absorption band, summation was carried out over 9 channels. In all the other cases the step was  $0.97 \text{ cm}^{-1}$ . The main contribution to the inaccuracy of determining the band intensities comes from the uncertainty in background subtraction.

The tabulated data suggest that irradiation decreases both the total concentration of  $\text{UO}_2\text{F}_2$  in solution and the proportion of the uranyl complexes containing one or two  $^{18}\text{O}$  atoms, and in this situation the  $[\text{}^{16}\text{O-U-}^{16}\text{O}]^{2+}$  concentration in solution can even increase. Notably, the content of  $[\text{}^{16}\text{O-U-}^{18}\text{O}]^{2+}$  in solution decreases during photoreduction more rapidly than that of  $[\text{}^{18}\text{O-U-}^{18}\text{O}]^{2+}$ .

We attempted to estimate the validity of this observation by comparing the rates at which the contents of the  $[\text{}^{16}\text{O-U-}^{18}\text{O}]^{2+}$  and  $[\text{}^{18}\text{O-U-}^{18}\text{O}]^{2+}$  species decrease during irradiation. To this end, we determined the ratios of the areas of the absorption bands

$S_1/S_2$  in the IR spectra of the samples obtained from the  $\text{UO}_2\text{F}_2$  solutions before and after irradiation (see Table 2). These data are listed below (error of  $1\sigma$ ).

Experiment no.	Before irradiation	After irradiation
1	$2.19 \pm 0.04$	$1.82 \pm 0.06$
2	$2.0 \pm 0.1$	$1.5 \pm 0.2$
3	$2.19 \pm 0.04$	$1.80 \pm 0.05$
4	$2.53 \pm 0.03$	$2.32 \pm 0.06$
5	$2.53 \pm 0.03$	$2.45 \pm 0.06$
6	$2.53 \pm 0.03$	$2.41 \pm 0.08$
7	$2.53 \pm 0.03$	$2.35 \pm 0.05$
8	$2.53 \pm 0.03$	$2.37 \pm 0.05$

These data suggest that the effect of interest can be revealed the more reliably, the higher the enrichment in  $^{18}\text{O}$ , since the areas of intense bands can be determined more precisely than those of weak bands.

Of much importance are the conditions in which the  $[\text{}^{16}\text{O-U-}^{18}\text{O}]^{2+}$  species of uranyl exhibits abnormal behavior when irradiated in solutions. When a saturated solution of  $\text{UO}_2\text{F}_2$  is diluted, the  $S_1/S_2$  ratio changes and approaches the initial value. In saturated  $\text{UO}_2\text{F}_2$  solutions diluted by a factor of 2, the isotope effect is not manifested at all. For the solutions diluted by 30%,  $S_1/S_2$  is equal to 3–5% (experiment nos. 5 and 6) but does not exceed  $2\sigma$ . Saturated (experiment no. 4) and diluted by 10% (experiment nos. 7 and 8) solutions exhibit the effect of 7–9%, and  $S_1/S_2$  exceeds  $2\sigma$ . In experiment nos. 1 and 3, the ratio of the areas of the  $\nu_{\text{as}}$  bands of the  $[\text{}^{16}\text{O-U-}^{18}\text{O}]^{2+}$  and  $[\text{}^{18}\text{O-U-}^{18}\text{O}]^{2+}$  species changes by  $\sim 20\%$ , which exceeds  $3\sigma$ . The  $\text{UO}_2\text{F}_2$  solutions in these experiments are supersaturated by a factor of approximately 2. Although the largest effect (33%) was observed in experiment no. 2, the enrichment in  $^{18}\text{O}$  was estimated at  $\sim 17\%$ , and this affected the accuracy of determining the bands areas. Therefore, in this experiment the effect of interest is revealed less reliably (the change in the  $S_1/S_2$  ratio does not exceed  $2\sigma$ ). In solutions containing  $\sim 1200 \text{ mg ml}^{-1}$   $\text{UO}_2\text{F}_2$ , which is thrice the solubility, the effect is not observed.

We believe that these statistical data confirm the existence of the isotope effect for saturated and supersaturated isopropanol solutions of  $\text{UO}_2\text{F}_2$ . The effect consists in that the content of the  $[\text{}^{16}\text{O-U-}^{18}\text{O}]^{2+}$  species in solution decreases with photoreduction of uranyl more rapidly than that of  $[\text{}^{18}\text{O-U-}^{18}\text{O}]^{2+}$ .

The content of  $[\text{}^{16}\text{O-U-}^{18}\text{O}]^{2+}$  and  $[\text{}^{18}\text{O-U-}^{18}\text{O}]^{2+}$  species can decrease owing both to uranyl reduction and oxygen exchange between uranyl and water, catalyzed by  $[\text{UO}_2]^+$  and occurring in solution simultane-

ously with the reduction of uranium. Let us analyze the possible contributions from the oxygen exchange and uranyl reduction to the behavior of the isotopic species of uranyl that we observed.

The oxygen exchange is evident from an increase in the  $[\text{}^{16}\text{O-U-}^{16}\text{O}]^{2+}$  concentration against a decrease in the total uranium concentration under irradiation of the solutions (see above).

As shown in [9, 10], the  $[\text{UO}_2]^+$  group formed from photoreduction of uranyl catalyzes the oxygen exchange of uranyl by the electron exchange reaction

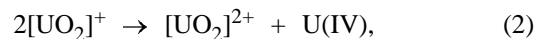


The oxygen exchange involves the uranyl groups that were not optically excited. Under favorable conditions, the number of the reaction events in such a chain process of electron transfer can reach  $\sim 10^3$  and over. At the  $\text{H}^+$  concentration that we chose, both one and two oxygen atoms in the uranyl group can be involved in the exchange [10].

In the case of two-oxygen exchange, the concentrations of the both isotopic species should decrease at identical rates. In the case of one-oxygen exchange, however, the concentration of the  $[\text{}^{16}\text{O-U-}^{18}\text{O}]^{2+}$  species will decrease more slowly than that of  $[\text{}^{18}\text{O-U-}^{18}\text{O}]^{2+}$ , since the statistical probability of exchange of one  $^{18}\text{O}$  atom for the former species is 2 times lower than that for the latter. Also, the  $[\text{}^{16}\text{O-U-}^{18}\text{O}]^{2+}$  content is replenished owing to the exchange of  $[\text{}^{18}\text{O-U-}^{18}\text{O}]^{2+}$ .

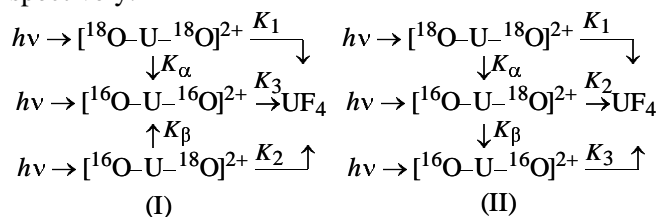
Thus, the existing views on the oxygen exchange in uranyl fail to explain the effect that we observed.

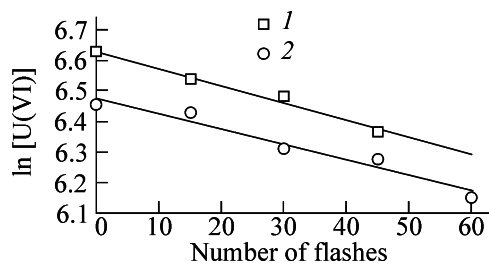
The second process responsible for a decrease in the content of  $^{18}\text{O}$  in  $\text{UO}_2\text{F}_2$  is reduction of  $[\text{UO}_2]^{2+}$  to U(IV), yielding insoluble  $\text{UF}_4$ . In alcoholic solutions U(VI) can be formed by disproportionation



as well as by two-electron reduction of the photoexcited uranyl with alcohol [11, 12].

Taking into account the exchange pathway, photoreduction can be represented by schemes (I) and (II) for the two- and one-oxygen exchange pathways, respectively.





**Fig. 4.** Rate of photoreduction of  $\text{UO}_2^{2+}$  in isopropanol in relation to the isotope composition of oxygen in  $\text{UO}_2\text{F}_2$ . (1) Natural isotope composition of oxygen in  $\text{UO}_2\text{F}_2$  and (2) 42% enrichment in  $^{18}\text{O}$ . Regression equations: (1)  $y = -0.0056x + 6.6292$ ,  $R^2 = 0.9879$  and (2)  $y = -0.0051x + 6.4756$ ,  $R^2 = 0.9583$ .

Here  $K_1$ ,  $K_2$ , and  $K_3$  are the photoreduction rate constants, and  $K_\alpha$  and  $K_\beta$ , the oxygen exchange rate constants for the corresponding isotopic species of uranyl.

Photoreduction is a first-order reaction, and for solutions of unenriched uranyl its rate is described by the equation

$$d[\text{UO}_2^{2+}]/dt = -K_3[\text{UO}_2^{2+}]; \quad d \ln [\text{UO}_2^{2+}]/dt = -K_3.$$

The total reaction time is proportional to the number of flashes, since the time between the flashes is much longer than the reaction time. Thus, the slope of the plot of the logarithm of the uranium concentration vs. the number of flashes yields a nominal  $K_3$  value. Figure 4 presents these dependences for uranyl both enriched and unenriched in  $^{18}\text{O}$ . It is seen that the slopes of both plots are close, which suggests that the rate constants of the photoreduction of  $^{18}\text{O}$ -enriched and unenriched uranyl are close as well. This means that the isotope effect in photoreduction proper is, evidently, lacking [i.e., in schemes (I) and (II)  $K_1 = K_2 = K_3$ ].

Rofer-DePoorter and DePoorter [13] studied the photochemical behavior of  $^{18}\text{O}$ -enriched uranyl fluoride in methanol. They also observed no differences in the quantum efficiency of photoreduction for different isotopic species of uranyl upon illumination of the solutions with a xenon pulse lamp and a laser at the generation wavelengths of 455 and 448 nm. They could not monitor the behavior of individual uranyl species, but observed a general decrease in the content of  $^{18}\text{O}$  in  $\text{UO}_2\text{F}_2$ . They explained the depletion of  $\text{UO}_2\text{F}_2$  in  $^{18}\text{O}$  in photoreduction under the conditions of completely suppressed, in their opinion, oxygen exchange by a difference in the extinctions of the  $\text{UO}_2\text{F}_2$  solutions differing in the isotope compositions of oxygen.

Figure 1 shows that, in our case, enrichment of  $\text{UO}_2^{2+}$  in  $^{18}\text{O}$  weakly affects the absorption of the  $\text{UO}_2\text{F}_2$  solution. Therefore, the difference in the reduction rates cannot be explained by different absorption coefficients of the isotopic species of uranyl. This fact suggests that other factors must be responsible for accelerated escape of the  $[\text{}^{16}\text{O}-\text{U}-\text{}^{18}\text{O}]^{2+}$  groups from solution.

As known,  $\text{UO}_2\text{F}_2$  is virtually nondissociated in aqueous solutions and tends to dimerize [14]. In non-aqueous and aqueous-organic solutions,  $\text{UO}_2\text{F}_2$  often exhibits higher degrees of polymerization even in the presence of ligands forming strong complexes, such as phosphine oxides, amides, etc. [15–19]. For example, the benzene-soluble complex of  $\text{UO}_2\text{F}_2$  with tributylphosphine oxide is a hexamer [15]; a complex of  $\text{UO}_2\text{F}_2$  with trioctylphosphine oxide also has a polymeric structure [16]. A complex with dimethyl sulfoxide is also a coordination polymer [17]. Antipyrine and dimethylformamide form polymers with  $\text{UO}_2\text{F}_2$  [17]. Urea [18] and hexamethylphosphoric triamide [19] form dimeric complexes.

We think that saturated isopropanol solutions also contain polymers (dimers) of  $\text{UO}_2\text{F}_2$ . In this case, the time dependence of the logarithm of the total concentration of U(VI) remains linear, while the changes in the concentrations of each isotopic species will be described by more complex equations than schemes (I) and (II). Since excitation causes reduction of only one  $\text{UO}_2^{2+}$  group, the excitation energy is eventually localized on one of the molecules constituting the polymer. Our experiments suggest that the photoreduction more often involves specifically the  $[\text{}^{16}\text{O}-\text{U}-\text{}^{18}\text{O}]^{2+}$  group. Such behavior of the latter can be explained by the fact that, when one  $^{16}\text{O}$  atom is replaced by an  $^{18}\text{O}$  atom in uranyl, the symmetry of the vibrational Hamiltonian of the uranyl group decreases from  $D_{\infty h}$  to  $C_{\infty v}$ . Therefore, such group predominantly accepts excitation during nonradiative energy exchange within the polymer.

#### ACKNOWLEDGMENTS

The authors are grateful to L.G. Mashirov for assistance in carrying out the spectrometric analysis.

#### REFERENCES

1. Burrows, Y.D. and Kemp, T.J., *Chem. Soc. Rev.*, 1974, vol. 3, no. 2, pp. 139–165.
2. Matsushima, R. and Sakuraba, Sh., *J. Am. Chem. Soc.*, 1971, vol. 93, p. 5421.

3. Rabinowitch, E. and Belford, R.L., *Spectroscopy and Photochemistry of Uranyl Compounds*, New York: Macmillan, 1964.
4. Mikhalev, V.A. and Suglobov, D.N., *Radiokhimiya*, 1992, vol. 34, no. 3, p. 1.
5. Mikhalev, V.A. and Suglobov, D.N., *Radiokhimiya*, 1993, vol. 35, no. 5, p. 1.
6. Calvert, J.G. and Pitts, J.N., *Photochemistry*, New York: Wiley, 1966. Translated under the title *Fotokhimiya*, Moscow: Mir, 1968, p. 625.
7. Savvin, S.B., *Organicheskie reagenty gruppy arsenazo* (Organic Reagents from the Arsenazo Group), Moscow: Atomizdat, 1971, p. 255.
8. Gaziev, S.A., Gorshkov, N.G., Mashirov, L.G., and Suglobov, D.N., *Radiokhimiya*, 1984, vol. 26, no. 3, p. 316.
9. Gordon, G. and Taube, H., *J. Inorg. Nucl. Chem.*, 1961, vol. 16, p. 272.
10. Gasiev, S.A., Gorshkov, N.G., Mashirov, L.G., and Suglobov, D.N., *Inorg. Chim. Acta*, 1987, vol. 139, p. 345.
11. Bell, J.T. and Buxton, S.R., *J. Inorg. Nucl. Chem.*, 1975, vol. 37, p. 1469.
12. Bell, J.T. and Billings, M.R., *J. Inorg. Nucl. Chem.*, 1975, vol. 37, p. 2049.
13. Rofer-DePoorter, C.K. and DePoorter, G.L., *J. Inorg. Nucl. Chem.*, 1978, vol. 40, p. 2049.
14. Mikhalev, V.A. and Suglobov, D.N., *Radiokhimiya*, 1992, vol. 34, no. 3, p. 9.
15. Vdovenko, V.M., Skoblo, A.I., and Suglobov, D.N., *Zh. Neorg. Khim.*, 1967, vol. 12, no. 10, p. 2863.
16. Vdovenko, V.M., Kovaleva, T.N., Kanevskaya, N.A., and Suglobov, D.N., *Radiokhimiya*, 1974, vol. 16, no. 1, p. 66.
17. Shchelokov, R.N., Orlova, N.M., and Podnebesnova, G.V., *Koord. Khim.*, 1975, vol. 1 no. 1, p. 119.
18. Mikhailov, Yu.N., Ivanov, S.B., Orlova, N.V., et al., *Koord. Khim.*, 1976, vol. 2, no. 11, p. 1570.
19. Shchelokov, R.N., Tsivadze, A.Yu., Orlova, N.V., and Podnebesnova, G.V., *Inorg. Nucl. Chem. Lett.*, 1977, vol. 13, no. 8, p. 375.