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THE ABSORPTION SPECTRA OF U^{4+} IONS IN ACID SOLUTIONS

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This paper presents the experimental results of the absorption measurements in the visible region of the U^{4+} ions in hydrochloric, phosphoric and sulfuric acid solutions. The absorption spectrum of the U^{4+}: H_3PO_4 in the region 420–2100 nm is recorded and the quantum - mechanical terms are described.

I. INTRODUCTION

The absorption spectrum of the U^{4+} is one of the most studied of all the actinide elements. This is because its compounds are readily available and it should have a relatively simple spectrum since it contains only two 5f electrons. Much work has been done on the absorption spectra of crystals containing tetravalent uranium, less on the solutions and comparatively little work has been carried out on glasses doped with uranium oxides.

The optical properties of alkali-alumino-phosphate (AAP) glasses with uranium were also investigated [1–3]. In these works, it was necessary to explain the luminescence of these green AAP glasses, while only the luminescence of yellow uranium glasses has been known so far. But the published absorption and luminescence spectra of the uranium glasses, due to the overlap of the absorption bands of the individual oxidation states of uranium, did not allow us to decide which oxidation states were formed in the investigated glasses. Therefore, to find the typical features and the positions of the characteristic bands of the individual oxidation states of uranium, which are not dependent on the chemical composition of the host material, we have paid attention to the optical measurements of solutions containing uranium in various oxidation states, because it was not difficult to prepare these solutions. The most suitable solutions for our purpose would be water solutions of metaphosphoric acid. However, these solutions are unstable [4] and transform into the solutions of orthophosphoric acid. So we investigated directly

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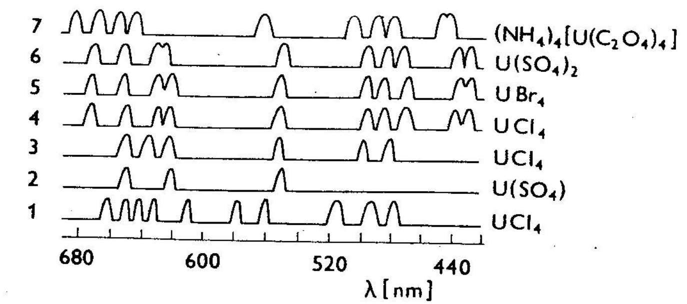

Fig. 1. Absorption spectra of the tetravalent uranium salts (curves: 1–3 from Ref. [7]: 4–7 from [10]).

the yellow water solution of the H_3PO_4 acid with $UO_2(NO_3)_2.6H_2O$. These yellow solutions illuminated by the mercury lamp with U G 5 filter turn green [5]. So the explanation of this photochemical reaction faced us with the problems of the absorption spectra of U^{4+} : H_3PO_4 and U^{4+} ions in other acid solutions, which are presented in this work.

The first measurements of the absorption spectra of water solutions of tetravalent uranium ions were recorded by Kato [6], Eprheim and Mezener [7]. They identified from three to seven absorption bands in the visible region shown in Fig. 1—curves 1–3. However, the spectrum of U^{4+}: HCl, observed in the region 400–700 nm by Satten et al. [8] consists of six bands only, while Veal et al. [9] observed nine bands. In the absorption spectra, shown in Fig. 1 curves 4–7, recorded by Ushatskij and Tolmatchev [10], ten bands were identified.

The measurement of U^{4+}: $HClO_4$ in the region 360–1300 nm was performed by Gruen and McBeth [11]. They recorded an identical spectrum with the absorption spectrum of U^{4+}: $DClO_4$, measured by Cohen and Carnall [12]. However, they extended their measurement up to 2300 nm. The interpretation of the spectra over the wavelength of 1700 nm, as the authors claim, is not unambigous, while in this region intensive D_2O bands are situated.

II. EXPERIMENTAL RESULTS

The absorption spectra, taken at room temperature, were measured with the aid of a registration spectrophotometer UV VIS Specord-Carl Zeis Jena in the region 400–800 nm and in the region 400–2100 nm with the spectrophotometer CF_4 - Optica Milano.

The IV oxidation state of uranium in acid solutions was prepared from the VI

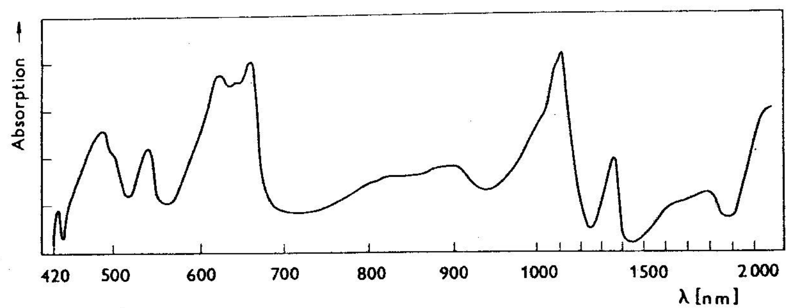

Fig. 2. Absorption spectrum of U^{4+} in H_3PO_4

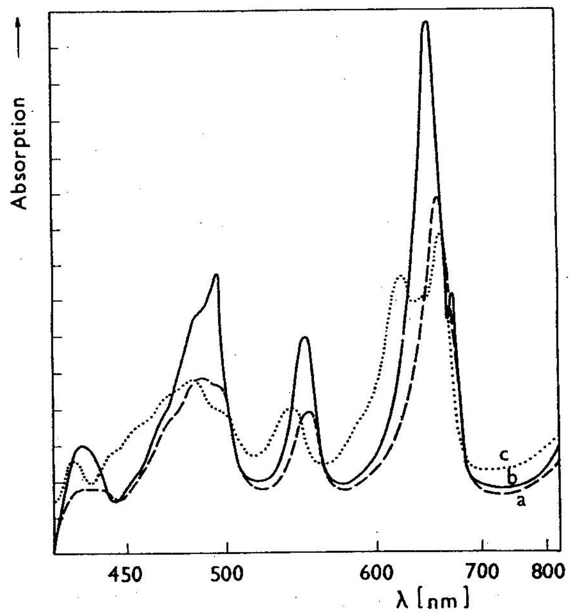

Fig. 3. Absorption spectrum of U^{4+} in : a) H_2SO_4; b) HCl; c) H_3PO_4.

oxidation states by:

1. electrolytic reduction
2. reduction with the metal zinc
3. photochemical reduction $UO_2^{2+} \rightarrow U^{4+}$ under the illumination of the lamp HBO - 200 W through the Schott filter UG 5.

Table 1

The energy-level diagram of U^{4+}: H_3PO_4

Position λ[nm]	Intensity [a.u.]	Assignment	Position λ[nm]	Intensity [a.u.]	Assignment
426	44		850	78	
444	55	$^3P_2$	882	86	$^3H_6$
457	86		905	88	
			925	67	
471	110				
483	124	$^1I_6$	974	125	$^3F_4$
500	100		997	156	
			1026	184	+
530	91	$^3P_1$	1192	203	$^3F_3$
540	106		1319	62	
			1376	94	
570	35	$^3P_0$			
583	86		1593	39	
			1656	48	
624	181	$^1G_4$	1768	57	$^3H_5$
640	173	+	1805	60	
660	196	$^1D_2$	1879	31	
793	68	$^3H_6$			

All these investigated spectra of U^{4+} ions that were prepared by the methods mentioned above were measured for all the observed solutions. As they were identical with the individual acid solutions, we not present them. However, this phenomenon can be seeen by comparison of the spectra of U^{4+} in H_3PO_4 shown in Fig. 2 and curve *c* in Fig. 3. The absorption spectrum of U^{4+}: H_3PO_4 in the region 420–2100 nm, Fig. 2 was obtained by the difference in the measurement of 0.02 M ⊙ $UO_2(NO_3)_2.6H_2O$ in 85% H_3PO_4 after illumination versus the solution before illumination. The position of the observed energy level and their assignment in $^{2S+1}L_J$ symbols are given in Tab. 1. The results of the absorption measurements of U^{4+} in: 25% H_2SO_4 - curve *a*, 3.6% HCl curve *b* and 85% H_3PO_4 - curve *c*, prepared by reduction with zinc in the metal state, are reproduced in Fig. 3 and tabulated in Tab. 2.

III. DISCUSSION

It has been known that the absorption spectra of tetravalent uranium arise from transition within a 5f shell of the ions. The $5f^2$ system of U^{4+} would be

Table 2

Absorption spectrum of U^{4+} in acid solutions

U^{4+}: H_2SO_4 λ[nm]	I [a.u]	U^{4+}: HCl λ[nm]	I [a.u]	U^{4+}: H_3PO_4 λ[nm]	I [a.u]
428	18			428	11
437	18	440	30	440	12
451	20	455	20	454	17
465	34	465	36	470	21
484	49	485	66	483	23
496	47	496	78	497	19
549	40	550	59	541	20
594	20	(612)	34	586	26
(632)	(52)			625	38
655	98	653	147	645	36
670	73	674	72	667	45

expected to yield an energy-level system of 13 lines. Twelve of them have been determined in the visible and infrared region in various host materials [12–15].

The observed absorption spectrum of U^{4+}: H_3PO_4, Fig. 2, consists of nine absorption bands. It is possible to explain this spectrum as the electron transition from the ground state $^3H_6$ to the excited electron levels. Tentative term notations in $^{2S+1}L_J$ symbols were assigned to the quantum states of U^{4+} ions, based upon the analogous $4f^2$ systems and a free-ion-like spectrum, predicted by Jorgensen [16] and also on the basis of a detailed study of the absorption spectra of crystals, solutions and glasses containing uranium [17].

The fact that the spin-orbit interaction for $5f^n$ electrons is larger than for $4f^n$ electrons resulting in a greater departure from the Russell-Saunders coupling of the former compared with the latter [18]. Another complicating factor is the greater spatial extension of the 5f wave functions, which results in a less perfect shielding from the electric field of the host material and in a larger Stark splitting of 5f compared with 4f electrons. In turn, this has a consequence in a greater degree of the mixing of free ion J values, which can be seen in Tab. 1 and Fig. 2 Each band except the maximum at 426 nm, consists of several subbands. With this overlapping it was difficult to obtain accurate values for the position and intensity of any single absorption band or transition band or transition with any reasonable accuracy.

From the comparison of the spectra of U^{4+} ions in the investigated acid solutions in Fig. 3, one may assess small changes, of the shape, position and intensity of the absorption bands. It is due to the effect of the medium on the spectrum of U^{4+} ions. The spectra in the region 560–700 nm showed that the largest splitting was observed for the phosphoric acid solution. Such splitting has not been published in solutions till now. The same splitting, however, was observed in this region in AAP glasses doped with uranium, investigated by Bohun et al: [1, 3, 17].

IV. CONCLUSIONS

From the absorption measurements given above it follows that the absorption of U^{4+} ions in investigated acid solutions arises from electronic transitions from the ground state $^3H_6$ to the excited states of tetravalent uranium.

The energy-level diagram of U^{4+}: H_3PO_4 and the quantum states assignment in the region 400–2100 nm were carried out.

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