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Abstract

Full Text

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PHYSICAL CHEMISTRY

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ABSORPTION SPECTRA OF CERTAIN COMPOUNDS OF TETRAVALENT URANIUM AT THE TEMPERATURE OF LIQUID NITROGEN

(Presented by Academician A. N. Frumkin on 7 I 1957)

1. A number of features of the absorption spectra of lanthanoid compounds in the solid and liquid states—for example, the extremely narrow absorption bands—are explained by the presence of unpaired electrons in the 4*f*-shell of these elements, while the bands in the infrared, visible, and near-ultraviolet regions are interpreted as transitions within the 4*f*-shell⁽¹⁾. Apparently, the nature of the absorption spectra of compounds of the actinoid series is the same; these spectra show considerable similarity to the spectra of lanthanoid compounds⁽²⁾. But this similarity, judging from the limited literature data, is not so striking for the first elements of the actinoid series, in particular for uranium, which in other physical and chemical properties also differs noticeably from the elements located closer to the middle of the actinoid series⁽²⁾.

Most of the data on the spectra of compounds of trivalent and tetravalent uranium (in which, in the 5*f*-shell, one may expect the presence of, respectively, three and two unpaired electrons) concern solutions, where the bands are considerably broader. In the solid state, only the reflection spectra of UF_4 , UCl_4 , UBr_4 , K_2UF_6 , K_2UCl_6 , $U(SO_4)_2$, $U(SO_4)_2 \cdot 4H_2O$, $U(SO_4)_2 \cdot 8H_2O$, and UCl_3 ⁽³⁾, and the absorption spectra of UF_4 , $NaUF_5$, KUF_5 , Na_2UF_6 (two modifications), UCl_3 , and UCl_4 ⁽⁴⁻⁶⁾, have been investigated.

2. In view of the above, we decided to investigate the absorption spectra of compounds of $U(IV)$ in the solid state at low temperature, in order to determine to what extent these spectra can be associated with the possible presence of the remaining two valence electrons, not participating in bonds, in the 5*f*-shell. In the present work we give the results of an investigation of the absorption spectra in the visible region of seven $U(IV)$ compounds*: $U(SO_4)_2 \cdot 8H_2O$, $U(C_2O_4)_2 \cdot 6H_2O$, $K_4[U(C_2O_4)_4] \cdot 5H_2O$, $K_2Sr[U(C_2O_4)_4] \cdot 8H_2O$, $Ca_2[U(C_2O_4)_4] \cdot 6H_2O$, $Ba_2[U(C_2O_4)_4] \cdot 8H_2O$,

and $Na_4[U(P_2O_7)_2] \cdot 8H_2O$, of which $Ca_2[U(C_2O_4)_4] \cdot 6H_2O$ was obtained for the first time.

3. The spectra obtained differ quite strongly from one another in character. Some of them (the spectra of $Na_4[U(P_2O_7)_2] \cdot 8H_2O$, $U(SO_4)_2 \cdot 8H_2O$) consist of very diffuse and broad bands with weak signs of structure. On the other hand, the bands of $U(C_2O_4)_2 \cdot 6H_2O$, $K_2Sr[U(C_2O_4)_4] \cdot 8H_2O$, and, especially, $Ca_2[U(C_2O_4)_4] \cdot 6H_2O$ and $Ba_2[U(C_2O_4)_4] \cdot 8H_2O$, broad at room temperature, at -196° split into a large number of predominantly narrow bands grouped in separate regions of the spectrum. We observed three such groups: in the regions from 6900–6700 to 6300–6200 Å (I), from 5700–5500 to 5400–5300 Å (II), and from 5200–5150 to 5050–4900 Å (III). It may be assumed that there is also a fourth group of bands in the region 8000–8500 Å, observed in the spectrum of $U(C_2O_4)_2 \cdot 6H_2O$.

* The author expresses deep gratitude to the staff of the chemical analysis laboratory of the Institute of Organic Chemistry of the USSR Academy of Sciences for determining the carbon and crystallization-water content in the synthesized preparations.

The wavelengths found for the indicated groups of bands agree with the data on the broad absorption bands of solution spectra^(3,7,8). Beginning with 4900–4800 Å, the character of the spectra changes noticeably. The bands become more diffuse and broader, and the number of fine-structure details decreases considerably. In this part of the spectrum there is observed one more group consisting of several broad bands in the region 4450–4250 Å, also found in the spectra of solutions⁽⁸⁾.

Each group consists of several intense and, for the most part, sharp bands located at the center (Fig. 1), a large number of weak but also predominantly sharp bands in the long-wavelength part, and comparatively broad bands against a background of appreciable intensity in the short-wavelength part. In those cases where the structure of individual groups of bands is poorly resolved or not resolved at all, in the short-wavelength part of the groups, instead of separate bands, a long “tail” is observed, slowly decreasing in intensity. Between the principal groups of bands, when thick layers of the preparations are photographed, a considerable number of weak bands is observed, whose intensity gradually decreases toward shorter wavelengths (Fig. 2). These features are very characteristic of the spectra investigated.

4. We believe that the most intense bands in each group correspond to purely electronic transitions from the ground state of the uranium ion. In this case the long-wavelength satellites of each group may be interpreted as purely electronic transitions from excited sublevels of the ground state of the uranium ion, arising as a result of removal of the degeneracy in J in the field of the crystal lattice. In the spectrum of $Ca_2[U(C_2O_4)_4] \cdot 6H_2O$, such long-wavelength satellites of the intense bands of the groups are separated from the latter by $157 \pm 4 \text{ cm}^{-1}$; in the spectrum of $Ba_2[U(C_2O_4)_4] \cdot 8H_2O$,

Figure 1

Figure 1: Figure 1

by $104 \pm 4 \text{ cm}^{-1}$ and $225 \pm 4 \text{ cm}^{-1}$, with the mean accuracy of determination of the positions of narrow and broad bands being respectively $\pm 2\text{--}4 \text{ cm}^{-1}$ and $\pm 5\text{--}7 \text{ cm}^{-1}$. The weak bands in the intervals between individual groups, which likewise copy the intense bands of the groups, may be assigned to transitions of the type $\nu_{\text{el}} + \nu_{\text{vib}}$, where ν_{vib} are the vibrational frequencies of $\text{C}_2\text{O}_4^{2-}$, $\text{P}_2\text{O}_7^{4-}$, SO_4^{2-} , and, possibly, H_2O . Such transitions have been observed in the absorption spectra of lanthanoid compounds⁽⁹⁾. Indeed, the ν_{vib} found in the spectra of $\text{Ca}_2[\text{U}(\text{C}_2\text{O}_4)_4] \cdot 6\text{H}_2\text{O}$ and $\text{Ba}_2[\text{U}(\text{C}_2\text{O}_4)_4] \cdot 8\text{H}_2\text{O}$ agree satisfactorily with the data on the infrared absorption spectrum of the related compound $(\text{NH}_4)_4[\text{U}(\text{C}_2\text{O}_4)_4] \cdot 6\text{H}_2\text{O}$ ⁽¹⁰⁾ (see Table 1).

Table 1

Found ν_{vib} , in cm^{-1}	Found ν_{vib} , in cm^{-1}	Frequencies of bands in the infrared absorption spectrum*
$\text{Ca}_2[\text{U}(\text{C}_2\text{O}_4)_4] \cdot 6\text{H}_2\text{O}$	$\text{Ba}_2[\text{U}(\text{C}_2\text{O}_4)_4] \cdot 8\text{H}_2\text{O}$	$(\text{NH}_4)_4[\text{U}(\text{C}_2\text{O}_4)_4] \cdot 6\text{H}_2\text{O}$
499 ± 5	500 ± 2	—
—	—	670 (weak)
810 ± 3	—	790 (strong)
—	—	900 (strong)
1165 ± 4 (?)	—	—
1308 ± 4	1293 ± 4	1320 (weak)
1430 ± 1 (?)	—	—
1650 ± 6	1630 ± 4	1630 (strong)

* Estimated from the graphical data presented in⁽¹¹⁾; the region below 600 cm^{-1} was not investigated.

The data from the analysis of other spectra are less reliable because of their greater diffuseness, and we do not present them. The bands and background in the short-wavelength part of the groups should apparently be assigned to combinations of electronic transitions with external vibrations of the crystal lattice.

To the article by K. P. Bunin, G. Z. Koval' chuk, and S. A. Fedorova, p. 281

graphite

ferrite

a *b*

Fig. 1

To the article by V. T. Aleksanyan, p. 333

Figure 1 Figure 2

Fig. 1. Second group of bands in the absorption spectra of thin layers of $\text{Ba}_2[\text{U}(\text{C}_2\text{O}_4)_4] \cdot 8\text{H}_2\text{O}$ and $\text{Ca}_2[\text{U}(\text{C}_2\text{O}_4)_4] \cdot 6\text{H}_2\text{O}$ (b)

Fig. 2. Absorption region between the first and second groups of bands in the spectra of $\text{U}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$ (a) and $\text{Ba}_2[\text{U}(\text{C}_2\text{O}_4)_4] \cdot 8\text{H}_2\text{O}$ (b)

5. According to Jørgensen's calculation⁽⁸⁾, the appearance of bands in the red, green, and blue regions of the spectra of U(IV) solutions (groups I, II, and III of bands in the spectra of crystals) is associated with transitions from the ground level 3H_4 of U(IV) $5f^2$ to the excited levels, respectively, 3F_4 (or 1G_4), 1D_2 , and 1G_4 (or 3F_4) of the same configuration. Jørgensen⁽⁸⁾ also gives the results of another calculation, based on Gruen's hypothesis⁽¹²⁾. In this case bands I, II, and III are interpreted, respectively, as transitions $^3H_4 \rightarrow ^3P_1$, $^3H_4 \rightarrow ^1I_6$, and $^3H_4 \rightarrow ^1D_2$. Our data cast doubt on both variants of the interpretation. As is known⁽¹¹⁾, in a crystalline field, depending on its symmetry, the degeneracy of levels with respect to J is partially or completely removed. The numbers of sublevels thereby formed, p_J , have been determined for fields of different symmetry by the method of group theory⁽¹¹⁾. Table 2 gives the expected ratio $p_I : p_{II} : p_{III}$ in fields of various symmetry for both variants of the interpretation of the U(IV) spectrum.

Table 2

Variant of interpretation	Expected ratio	Expected ratio	Expected ratio
	$p_I : p_{II} : p_{III}$ in a field with cubic symmetry	$p_I : p_{II} : p_{III}$ in a field with hexagonal symmetry	$p_I : p_{II} : p_{III}$ in fields with tetragonal symmetry and lower
First	2 : 1 : 2	2 : 1 : 2	9 : 5 : 9
Second	1 : 6 : 2	2 : 9 : 3	3 : 13 : 5

The number of sublevels in the upper states of U(IV) can be judged from the number of intense bands in the corresponding groups of bands. According to our data, $p_I : p_{II} : p_{III} \simeq 2 : 2 : 1$, which contradicts both variants of the interpretation.

In the present communication we confine ourselves to noting the discrepancy between the data obtained and the attempts available in the literature to interpret the absorption spectra of U(IV) on the basis of the $5f-5f$ hypothesis. The

possible reasons will be set forth after publication of the remaining experimental data at our disposal.

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Note added in proof. After the manuscript had already been submitted for publication, a description of the synthesis of $\text{Ca}_2[\text{U}(\text{C}_2\text{O}_4)_4]6\text{H}_2\text{O}$ appeared in the literature ⁽¹³⁾.

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