

L. V. Volod'ko. The Spectra and Kinetics of the Luminescence of the Actinides. The spectral-luminescence properties of the compounds of actinides in di- and trivalent states can be interpreted relatively fully by using the analogy with the lanthanide compounds. When analyzing the spectra of the compounds of higher-valency actinides, such an approach is essentially limited. We can now consider as having been established the fact that the characteristics of a number of the physicochemical properties of these compounds are due to the participation of the f-shell electrons in the valence interactions, which is not valid for the elements of the preceding part of the periodic table. The types of classification of the electronic states of the compounds of the hexa- and pentavalent actinides proposed by a number of authors take into account in diverse degrees this distinctive feature of the valent interactions, but the application of their schemes to the interpretation of the electronic spectra meets with substantial disagreements between the results of the theoretical estimates and experiment. The correction of the indicated classifications is hindered by the absence of any data on the nature of the transitions between the various electronic states.

The absorption of light in the visible and near-ultraviolet regions of the spectrum by penta- and hexavalent actinides is mainly due to the excitation of the valence-shell electrons of the molecules. The spectra of this region resolve, under definite conditions, into several band series. Each of these series is due to transitions to electronic-vibrational levels of the individual excited states. The positions of the latter in the frequency scale are shifted relative to each other within the limits  $700\text{--}3000\text{ cm}^{-1}$ . The magnitude of the shift depends on the atomic number of the complexing ion, the structure of the coordination sphere, and the nature of the ligands<sup>[1]</sup>.

As has been shown in<sup>[2]</sup>, many distinctive features of the spectra of the compounds of actinides of higher valency are satisfactorily explained when the charge of the nucleus of the complexing ion is taken into account. This allows us to focus our main attention on the interpretation of the spectral-luminescent characteristics of uranyl compounds with a subsequent extrapolation of the results obtained to the isostructural compounds of the transuranium elements. This method is more preferable, especially in the investigation of luminescence characteristics, since it enables us to avoid the necessity of taking into account the effects connected with the high specific radioactivity of the transuranium elements.

The absorption spectra of the uranyl compounds in the  $20000\text{--}30000\text{ cm}^{-1}$  frequency range are formed by four line series superimposed on each other and washed out at room temperature into bands. There is at present no reliable criterion with the aid of which we can determine the series to which each line of the fine structure of the spectrum belongs. We used for this purpose the mirror-symmetry rule for absorption and luminescence spectra, which has been shown under diverse experimental conditions to be applicable to the uranyl compounds<sup>[3]</sup>. The reliability of the division of the lines into series was checked by measuring their dichroism at  $77^\circ\text{ K}$ . The data obtained were used to compute the transition oscillator strengths. The results of

Transition oscillator strengths  
( $f \times 10^5$ ) of the crystals of  
uranyl compounds at  $77^\circ\text{ K}$

| Electron-transition spectrum | $\text{Cs}_2\text{UO}_2\text{Cl}_4$ | $\text{CsUO}_2(\text{NO}_3)_3$ | $\text{NH}_4\text{UO}_2(\text{NO}_3)_3$ |
|------------------------------|-------------------------------------|--------------------------------|---|
| 1                            | 0.76                                | 1.02                           | 0.51                                    |
| 2                            | 3.04                                | 8.37                           | 7.39                                    |
| 3                            | 7.50                                | 8.29                           | 5.56                                    |
| 4                            | 5.39                                | 5.61                           | 5.02                                    |

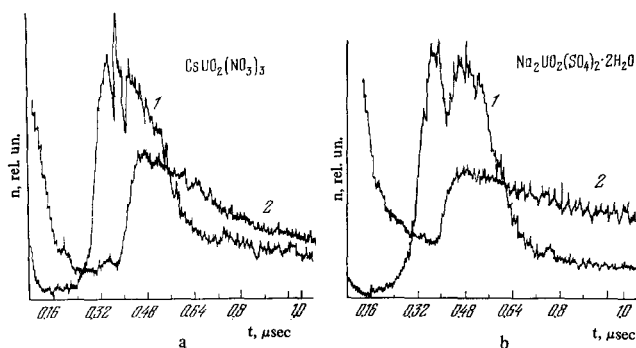
the computation are presented in the table, where the numbering of the transitions begins from the long-wave side of the absorption spectrum.

Comparison of the results of the separation of the integral spectra of a number of crystals revealed the following distinctive features of the transitions in different excited electron states. The value of the oscillator strength of the transition to the 4th excited state is not influenced by such strong factors as the substitution of the ligands in the coordination sphere of the uranyl ion, the substitution of the second cation, and a change in the symmetry of the crystal field. The probabilities of transition to the three lower-lying excited electronic states manifest significant changes under these conditions, the nature of the variations being different for each of them. It follows that the electron states under consideration are characterized by different symmetry and, consequently, contrary to common opinion, they cannot be considered as the components of a triplet.

To reveal the nature of the transitions between the excited electron states, the kinetics of the luminescence of the crystals of uranyl compounds was recorded in  $10^{-9}\text{--}10^{-6}$ -sec time interval using a statistical method<sup>[4]</sup>. The time variation of the intensity of the luminescence excited by the light pulse of an electric discharge in oxygen (duration of the flash = 3 nsec) is shown in the figure. An exponential luminescence process of mean duration of the order  $10^{-8}$  sec directly follows the excitation pulse. This coincides with the results of measurements of the duration of the luminescence of uranyl compounds carried out by Gaviola<sup>[5]</sup> in 1927 with the aid of an optical "fluorescope" in Kerr cells. These measurements have up till now been presented as a curiosity.

Clearly expressed in the luminescence kinetics is a dark break of duration  $2.4 \times 10^{-7}$  sec, when the radiation was observed "by reflection," and  $4 \times 10^{-7}$  sec, when it was observed "by transillumination." The duration of this pause is the same for all the crystals of the uranyl compounds we have studied, and determines the process whereby the energy is redistributed among the excited electronic states of the uranyl ion. Hence it follows that transitions between these electronic states, like those between the ground and the first excited states, are forbidden. The luminescence kinetics observed "by reflection" is different from the kinetics observed "by transillumination." This difference does not amount to a manifestation of secondary luminescence, or a migration of the excitation energy; it is of more complex nature. The number of maxima on the luminescence curve depends on the degree of imperfection of the crystal and is different for different crystals.

Since the luminescence spectra<sup>[6]</sup> and the quantum



Kinetics of the luminescence of a) cesium uranyl nitrate and b) sodium uranyl sulfate at room temperature. The luminescence was detected 1) "by reflection" and 2) "by transillumination."

yield<sup>[7]</sup> of uranyl compounds depend on the wavelength of the exciting light, the above-presented results indicate that in the present case the luminescence kinetics is determined by the mechanism underlying the establishment of the equilibrium energy distribution over the crystal as a whole, and not by the nature of the elementary radiator. The latter determines the kinetics of an earlier afterglow phase, which is characteristic, as can be seen from the data presented, of an electric dipole radiation. This radiation makes a relatively small contribution to the light sum, and this corresponds to a small value of the coefficient of absorption of light in the spectral region corresponding to the first excited electronic state.

The above-discussed observations confirm the assertion made previously<sup>[8]</sup> that the spectral-lumines-

cent characteristics of the class of substances being considered are determined not by the properties of an isolated complexing ion, but by the entire set of the interacting structural elements of its surroundings. As has been shown in<sup>[9]</sup>, the classification of the electronic states of the uranyl compounds, proposed on the basis of this premise<sup>[10]</sup>, possesses the necessary generality for the interpretation of the spectra of specific substances.

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<sup>4</sup> L. V. Volod'ko, M. I. Demchuk et al., *Zh. Prikl. Spekt.* **16**, 1001 (1972).

<sup>5</sup> E. Z. Gaviola, *Zs. Phys.* **42**, 853, 862 (1927); E. Z. Gaviola and P. Pringsheim, *ibid.* **43**, 384 (1927).

<sup>6</sup> V. L. Levshin and G. D. Sheremet'ev, *Zh. Eksp. Teor. Fiz.* **17**, 204 (1947).

<sup>7</sup> M. N. Alentsev, *Tr. FIAN SSSR* **5**, 339 (1950).

<sup>8</sup> B. I. Stepanov, *Zh. Eksp. Teor. Fiz.* **21**, 1153 (1951).

<sup>9</sup> C. Gorller-Warland and L. G. Vanquickenborne, *J. Chem. Phys.* **54**, 4178 (1971).

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