ANALYSIS OF THE LATENT STRUCTURE OF LUMINESCENCE AND ABSORPTION SPECTRA OF THALLIUM COMPLEXES

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Comprehensive investigations of luminescence, excitation, and absorption spectra as well as of the luminescence kinetics of a frozen LiCl–Ti⁺ solution are carried out. It is established that the luminescence spectrum consists of four components. One component is caused by luminescence of the matrix and the remainder by luminescence of one luminescence center, namely, by the saturated complex of thallium TiCl₄(H₂O)Cl. The absorption spectrum consists of three components. Their parameters have been evaluated. Each component of the luminescence spectrum is excited in several components of the absorption spectrum. It is found that the luminescence spectrum components and their intrinsic absorption bands are located differently on the frequency axis. These data are similar to those obtained for other activated solutions of electrolytes.

Keywords: thallium, solution, complex, spectrum, luminescence, absorption, excitation, structure, mercury-like ion.

One must study the structure of the luminescence spectrum (LS) and absorption spectrum (AS) of complexes of mercury-like ions in aqueous solutions of electrolytes in order to establish energy states and the interrelation between them and to construct an adequate energy model of luminescence centers (LC). This is important both for insight into the processes occurring in this type of LC, especially in connection with spectroscopic manifestation of f-electron collapse [1, 2], and for evaluation of the possibilities of producing light amplification on these objects.

In the present work we investigate the structure of the LS and AS of a LiCl–Ti⁺ frozen solution, which differs from other electrolyte solutions activated with mercury-like ions at both low and room temperatures. Investigations of this solution are made more complicated because the spectral components in the complex AS and LS overlap appreciably, so that externally these spectra appear as structureless (Fig. 1a), and the LS depends relatively weakly on the exciting light frequency νexc. Therefore, to establish the AS and LS structure, we have carried out comprehensive investigations of the AS, LS, excitation spectra (ES), and the luminescence kinetics. To decrease the probability of nonradiative transitions through energy barriers between excited electronic-vibrational states and thereby to decrease their interrelation, the investigations were conducted at nitrogen temperature. The concentrations of the solution components amounted to \( C_{Ti} = 1.7 \times 10^{-3} \) mole/liter and \( C_{Li} = 7.5 \) mole/liter. Under these conditions the solution was in a glassy optically homogeneous state.

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The ES and LS were recorded upon luminescence excitation by hydrogen-deuterium lamp (DL)(D) radiation liberated by a DMR-4 monochromator, the AS was recorded by a KSVU-23 spectral system, and the luminescence kinetics was registered directly as oscillograph traces upon excitation by pulses of the fourth harmonic of a YAG-Nd$^{3+}$ laser ($\tau_i = 10$ nsec, $v_{\text{exc}} = 37,750$ cm$^{-1}$). The luminescence radiation was isolated by a DMR-4 monochromator and recorded by an 18ELU-FM fast photomultiplier and an S8-12 storage oscilloscope with a total time resolution of $\tau_i = 10$ nsec.

The number of LS components and their parameters were established from the results of treatment of a set of the LS recorded at different excitation frequencies ($v_{\text{exc}} = 37,600$, 38,500, 39,950, 41,150, 43,000, and $45,100$ cm$^{-1}$). We used the Alentsev–Fock method [3], the UPOS program of processing spectra [4], and an analysis of the second derivative of these spectra. We carried out our investigations in the following sequence. Using the second derivatives of the LS (Fig. 1b), we established the total number of components (four) and approximate values for the frequencies of their maxima. These frequencies were refined by the Alentsev–Fock method, and the contours of the components $L_1$–$L_4$ were preliminarily determined. Using the UPOS program we further refined the component parameters by means of the criteria of the best agreement for all the above-indicated excitation frequencies: the LS obtained from the experiment and calculated from the contours of the components $L_1$–$L_4$ (Fig. 1a), the second derivatives of these spectra (Fig. 1b), and the LS ratios obtained at different $v_{\text{exc}}$ for the calculated and experimental spectra (Fig. 1c).

The simultaneous use of the three criteria substantially increased the reliability of the decomposition of the LS, since each of them is unequally sensitive to the parameters of different components. The total contours of the LS components is sensitive to the parameters of the central and most intense components, while the ratio of the LS for different $v_{\text{exc}}$ is sensitive to the parameters of the peripheral components. The second derivative was used for refining the half-widths and for the final fitting of the other parameters of the components. As a result, the relative error of reproduction of the entire set of the recorded LS amounted to no more than 2% near