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Abstract

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ON THE PROBLEM OF THE SYSTEMATICS OF THE ELECTRONIC STATES OF URANYL COMPOUNDS

The application of the mirror-symmetry rule (1) to the electronic-vibrational absorption and emission spectra of uranyl compounds in the frequency region 20 000–30 000 cm^{-1} (2–4) makes it possible to assign the absorption-spectrum lines of crystals of these objects at low temperatures to optical transitions into four excited electronic states. Absorption in the ultraviolet region is due to transitions into two further states ($\nu \sim 34\,000$ and $48\,000$ cm^{-1}), which, in the opinion of McGlynn and Smith (5), also belong to the uranyl ion. Meanwhile, it is well known that precisely these bands are characteristic, for example, of the nitrate ion ($n \to \pi^*$- and $\pi \to \pi^*$-transitions) (6). Numerous results of our experimental spectral investigations confirm the viewpoint that the last two light-absorption bands belong to the anions.

It follows from the foregoing that, for the systematics of the electronic spectra of uranyl compounds, it is necessary to consider four electronically excited states, and not 5, as McGlynn and Smith do (5). The manifestation in electronic-vibrational spectra of transitions to sublevels of ligand vibrational energy (7) in principle requires seeking solutions to the problem posed on the basis of the symmetry of the structure of uranyl complexes. Obviously, at the present stage of research one may restrict oneself to an analysis of the uranyl group coordinated in the equatorial plane by 6 atoms, regardless of whether the latter are isolated addends or are constituents of polyatomic ligands. In the real structures of uranyl compounds, regular dodecahedral coordination of the uranium atoms is practically not realized. Therefore one may consider changes in the electronic-vibrational spectra of uranyl compounds upon changes in their structure from the standpoint of a lowering of the symmetry of the immediate environment of the uranyl ion. One may suppose that the electronic shell of uranyl, free from external influences deforming its coordination sphere, belongs to the point group D_{6h} and is due to the participation of electrons of the uranium atom not only in bonds with the axial oxygen atoms of uranyl, but also in covalent interactions with ligands coordinated in the equatorial plane of this group. The presence in uranyl compounds of 4 electronic states of different symmetry types with a forbidden character of their optical excitation also agrees well with the irreducible representations of this point group. Comparing the characters of the

Fig. 1

Figure 1: Fig. 1

irreducible representations of the point groups D_{6h}, S_6, D_{3h}, C_3, and C_s, and analyzing changes in the absorption spectra upon variations in the structure of complexes, one can make certain assumptions about the symmetry types of the excited electronic states of the uranyl ion.

The ground electronic state of uranyl, without any doubt, belongs to the totally symmetric representation of this point group. The character of the changes in the spectrum of the first excited electronic state upon lowering the symmetry of uranyl complexes and the high degree of polarization of its principal lines ([8]) make it possible to assign this state to the symmetry type B_{2g}. The second excited state is affected to a relatively lesser degree by changes in the structure of the complexes, up to the transition to

groups of lower symmetry. The strong depolarization of the principal absorption bands and their splitting in a magnetic field [9] indicate quite unambiguously that this electronic state belongs to the symmetry type E_{1g}.

The disappearance of the covalent character of the coordination bonds upon transition of the uranyl group to the third excited electronic state makes its classification difficult. The corresponding region of the absorption spectrum is usually characterized by the lowest intensity. A substantial violation of the prohibition on optical excitation of this state is observed only upon transition to complexes of lower symmetry groups, which agrees best with assigning it to the type A_{1g}. There is the least information about the fourth excited electronic state. Strong superposition on this region of the absorption spectra of uranyl compounds of electronic transitions between ligand energy levels masks its behavior when the structure of the complexes is changed. Comparison of the spectra of crystals and solutions indicates that the symmetry type of the fourth excited electronic state should be chosen from among three irreducible representations: A_{1u}, B_{1u}, or B_{2u} of the point group D_{6h}. It is not possible at present to give preference to any one of them.

Fig. 1

In Fig. 1 two schemes of the energy levels of the uranyl nitrate complex are compared for symmetry of the uranyl group D_{6h}, of which *a* was proposed by McGlynn and Smith on p. [10], and *b* by us. Despite the existing ambiguities (classification of the fourth electronic state), scheme *b*, as the result of a generalization of the experimental facts available at present, can serve as a starting point for deciphering the electronic structure of uranyl compounds.

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