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Abstract

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ON THE INTERPRETATION OF THE ELECTRONIC AND VIBRATIONAL ABSORPTION SPECTRA OF URANYL NITRATES

Numerous works have been devoted to the interpretation of the electronic and vibrational spectra of uranyl compounds. In this connection attempts are usually made to establish an unambiguous relationship between the frequencies of the infrared spectra and the "fine" structure arising in the electronic-vibrational spectra of crystals of uranyl salts at low temperatures. Analysis of the electronic spectra makes it possible to detect, for all uranyl salts, several fundamental frequencies approximately equal to 860, 940, and 210 cm^{-1} (^{1}). In the combination-scattering spectra of saturated solutions of a number of uranyl salts, the frequencies 860 and 210 cm^{-1} appear (^{2,3}). In the infrared spectra of all crystals and solutions of uranyl salts, a very intense absorption band was found in the region of 940 cm^{-1} (^{2,4}).

Analysis of these frequencies, taking into account the selection rules for a linear triatomic molecule, makes it possible to assign them to the symmetric and antisymmetric valence and deformation vibrations of the uranyl ion. The weak absorption band often observed in infrared spectra in the region of 860 cm^{-1} (^{2,4}), as well as the weak 940 cm^{-1} line in the combination-scattering spectrum (^{2,3}), indicate that the selection rules are not always obeyed strictly, owing to the considerable influence of the medium on the form of the uranyl ion.

The above interpretation of the frequencies 860, 940, and 210 cm^{-1} is now generally accepted. However, the remaining frequencies of the infrared spectra of uranyl salts have not yet received an unambiguous interpretation. According to A. N. Sevchenko and B. I. Stepanov (^{4}), in the infrared absorption spectra of uranyl salts, in addition to the fundamental vibrational frequencies of the ion UO_2^{2+}, overtones and combination frequencies of the fundamental vibrations appear. Ya. I. Ryskin et al. (^{5}) interpreted the infrared absorption spectra of ethereal and ketone solutions of uranyl nitrate on the basis of the vibrational frequencies of the free symmetric ion NO_3^-, which represents a point group D_{3h} and has four characteristic vibrational frequencies: 1050 cm^{-1} (inactive in the infrared spectrum); 830; 1390; and 720 cm^{-1}. The authors explain the deviation of the experimentally observed frequencies from the corresponding values characterizing the vibrations of the isolated ion NO_3^- by a lowering of the symmetry of the NO_3^- ion owing to the presence of a bond of increased strength between one of the oxygen atoms O′ of the anion and the uranyl ion. The formation of such a bond, in the authors' opinion, should cause a change in the vibrational frequency of the N—O′ bond, entailing a disturbance of the resonance between the vibrations of the N—O and N—O′ bonds. The latter causes splitting of the vibration with frequency 1390 cm^{-1} into two components, 1280 and 1250 cm^{-1}, and activation of the vibration with frequency 1050 cm^{-1}.

In the fluorescence spectra of uranyl compounds, along with the vibrational frequencies of the uranyl ion, vibrational frequencies of anions also appear (6). The latter makes it possible to suppose that the coincidence noted above of the vibrational frequencies of the uranyl ion in the electronic and vibrational spectra of uranyl salts will also extend to anion vibrations.

The frequencies of these vibrations in the fluorescence spectrum were established by Dicke and Duncan (6) by measuring the displacement of spectral lines upon substitution of nitrogen N^{14} by the isotope N^{15} in double cesium, potassium, and rubidium salts of uranyl nitrate. The values of these frequencies are given in Table 1. On the basis of these data we attempted to analyze the frequencies observed in the infrared absorption spectra of solutions of hexaaquodinitratouranyl and uranyl trinitrate in acetone. The uranyl trinitrate complex was obtained by mixing equimolar solutions of hexaaquouranyl nitrate and tetraethylammonium nitrate in acetone at room temperature. The formation of this complex was monitored from the electronic absorption spectra (7,8). The infrared spectra were recorded on an IKS-14 double-beam spectrophotometer at a concentration of the substance under study of 0.2 M and a layer thickness of 0.05 mm. The spectra of the compounds studied are shown in Fig. 1. It is evident from the figure that the indicated spectra differ from one another only by some redistribution of absorption intensity over the frequencies and by a slight shift of the bands. The frequency values of the maxima of the most intense absorption bands of uranyl trinitrate are given in Table 1.

Table 1

Frequencies, cm^{-1}	Frequencies, cm^{-1}	Frequencies, cm^{-1}
vibrations of the NO_3^- ion in the fluorescence spectrum of $CsUO_2(NO_3)_3$ (6)	maxima of absorption bands in the i.r. spectrum of uranyl trinitrate solution in acetone	absorption maxima in the i.r. spectrum of nitrate compounds with covalent bonding (9)
1706,72	1624	
1503,99	1510	1530—1480
1518,86		1530—1480
1277,51	1275	1290—1250

Frequencies, cm^{-1}	Frequencies, cm^{-1}	Frequencies, cm^{-1}
	1175	
	1122	
	1076	
	1025	1010–1020
	1010	1010–1020
	945	
	845	
	828	820–830
804,56	814	~ 800
804,56	797	~ 800
749,13	744	
739,11	734	
712,73	717	
712,73	705	

From a comparison of the data in the first and second columns of Table 1 it is evident that the frequency values of the vibrations of the NO_3^- ion obtained from fluorescence spectra coincide with a number of frequencies in the infrared spectrum. The latter should be assigned to vibrations of the same anion. The absorption band at 1624 cm^{-1} is assigned to deformation vibrations of the water molecule, and 945 cm^{-1} to antisymmetric stretching vibrations of the UO_2^{2+} ion.

On the basis of a study of the infrared spectra of a large number of ionic and covalent metal nitrates, Gatehouse et al. $^{(9)}$ came to the conclusion that strong absorption bands in the region 1530—1480 cm^{-1} in compounds containing NO_3-groups indicate the presence of covalent bonds between nitrate oxygen and the cation. This is connected with the fact that in ionic nitrates, ultimately, all $N—O$ bonds are equivalent, whereas in the case of covalent bonding of one of the oxygen atoms to the central metal atom this equivalence is disturbed. In this case there is no absorption band with frequency 1390 cm^{-1}, characteristic of the free nitro ion. In ionic nitrates the indicated bands were not detected. The frequencies of absorption bands characteristic of nitro compounds with covalent bonding according to Gatehouse are given in Table 1.

It follows from the data of Table 1 that in the infrared absorption spectra of uranyl nitrates, in addition to the vibrational frequencies of the UO_2^{2+} ion $^{(4)}$, a considerable number of frequencies belonging to vibrations of the NO_3^- anion are manifested. At the same time, the interpretation of these frequencies indicates the covalent character of the bond of the nitrate anion with the uranyl ion.

In contrast to the infrared spectra, the electronic absorption spectra undergo very strong changes upon formation of trinitrate

uranyl. Figure 2 shows the absorption spectra of solutions of hexahydrated uranyl dinitrate and uranyl trinitrate in acetone at room temperature. The

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

introduction of a third nitro group causes a strong increase in the absorption of four long-wavelength bands with maxima at 21404; 22114;

Fig. 1. Infrared transmission spectra of solutions of uranyl nitrates in acetone: **a** –dinitrate, **b** –trinitrate

Fig. 2. Electronic absorption spectra of a solution of uranyl dinitrate (1) and trinitrate (2) in acetone and of a single crystal of uranyl nitrate (3), as well as the polarized spectrum (4) and absorption dichroism (5) of a uranyl nitrate single crystal (χ –molar absorption coefficient, P –degree of polarization of the radiation, D –absorption dichroism)

22831 and 23545 cm^{-1}, whereas in the rest of the visible region of the spectrum no substantial changes occur. Sharp absorption bands also arise in the ultraviolet region, where continuous absorption is usually observed for all uranyl compounds.

Our experiments on the absorption dichroism and the dependence of the degree of polarization of fluorescence on the frequency of the exciting light (Fig. 2) indicate the presence of four electronic transitions in the investigated region of the spectrum. Analysis of the reasons for the absence of mirror symmetry in the experimentally observed absorption and emission spectra of uranyl compounds also leads to the conclusion that several excited electronic states of the uranyl ion exist [10]. Comparison of the absorption spectra of solutions of uranyl dinitrate and trinitrate in acetone with the spectra of aqueous and acidic solutions of uranyl nitrate, for which the first excited electronic state of the UO_2^{2+} ion is readily identified by means of the mirror-symmetry rule, shows that the strong changes observed in the absorption spectrum on going from uranyl dinitrate to uranyl trinitrate occur in the region of the second and fourth electronic transitions. It is possible that coordination of the third nitro group around the uranyl ion leads to a change in the symmetry of the absorbing center and to a weakening of the prohibition for the indicated electronic transitions.

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