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Abstract

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ON THE INTERPRETATION OF THE ABSORPTION SPECTRUM OF A CESIUM URANYL CHLORIDE CRYSTAL

Repeated attempts to interpret the complex structure of the absorption spectra of uranyl chloride crystals in the visible and near-ultraviolet regions of the spectrum at low temperatures have so far not been successful.

There are several points of view on the nature of the structure of the absorption bands. According to one of them (^1), the indicated structure is due to electron-vibrational transitions to the sublevels of a regular triplet. Proponents of another point of view (^2, ^3) connect the complex pattern of the absorption spectrum with electron-vibrational transitions to one triplet and several singlet states. In the authors' opinion, such an interpretation is doubtful, and in order to assess the reliability of one scheme or another it was necessary to study the absorption spectrum of the $CsUO_2Cl_4$ crystal in polarized light.

In the present communication an interpretation is given of the structural region of the absorption spectrum of a cesium uranyl chloride crystal at 77° K, consistent with that previously proposed by the authors for uranyl nitrate crystals (^{4}-6). A connection has also been established between the vibrational frequencies of the lower and upper excited electronic states. The crystals for the investigations were grown from slightly acidified saturated aqueous solutions of this salt by the method of free evaporation at constant temperature. Cesium uranyl chloride crystals belong to the monoclinic system; they are optically biaxial, negative. The optical indicatrix is elongated along the bisector of the obtuse angle. The specimens for investigation were cut in the form of plates parallel to the plane of the optical axes. Recording of the absorption spectra was carried out in linearly polarized light on the apparatus described in (^7), for two orientations of the specimen: the bisector of the acute angle parallel and perpendicular to the principal transmission plane of the analyzer. The direction of propagation of the light was perpendicular to the plane of the optical axes. Figure 1 gives the absorption spectra of the $CsUO_2Cl_4$ crystal for two components of the electric vector: **E** parallel and perpendicular to the bisector of the acute angle (b.a.a.). *a* and *b* are different regions of the absorption spectrum. A qualitative comparison of the two components of the crystal spectrum shows that in the component

Fig. 1. Absorption spectrum of a cesium uranyl chloride crystal at 77° K in polarized light. 1 $-E \perp$ b.o.u.; 2 $-E \parallel$ b.o.u.

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perpendicular to the bisector of the acute angle (*1*) the absorption spectrum is very rich, whereas in the parallel component (*2*) it is greatly simplified, which considerably facilitates the interpretation.

The purely electronic transition at 77° K has a frequency of 20 092 cm^{-1}, which coincides resonantly with the short-wavelength line of the luminescence spectrum. It is characteristic that the structure of the absorption spectrum and the polarization of the lines in the region of the first electronic transition coincide with the structure and polarization of the lines of the luminescence spectrum (ˆ8). This fact makes it possible to identify in the absorption spectrum all the lines belonging to the first excited electronic state.

Table 1 gives the frequencies of the purely electronic transitions and their differences from the frequencies of the absorption lines of the first groups of the series. An asterisk marks

lines repeated in subsequent groups of this series. The periodicity of the series includes combinations with the purely electronic transition of the totally symmetric stretching vibrations ν_1 of the uranyl ion in the excited state. In the region of the first electronic transition it is easy to find 6-7 repetitions of 716 cm^{-1}. The lines 20325, 20339, and 20366 cm^{-1} correspond to a combination of the purely electronic transition with the deformation vibrations ν_2 of the uranyl ion and with uranium-ligand vibrations. The difference between the indicated lines and the frequency of the purely electronic transition is 233, 247, and 274 cm^{-1}, respectively. The first frequency should apparently be assigned to a

Fig. 1. Absorption spectrum of a cesium uranyl chloride crystal at 77° K in polarized light. 1 $-E \perp$ b.o.u.; 2 $-E \parallel$ b.o.u.

uranium-ligand vibration, since its polarization coincides with the polarization of the purely electronic transition. The other two frequencies evidently correspond to deformation vibrations ν_2 of the uranyl ion, polarized perpendicular to the b.o.u. The weak line 20405 should most probably also be assigned to a combination of the purely electronic transition with the U—L vibration. The corresponding band in the luminescence spectrum is rather intense and is polarized perpendicular to the bisector of the acute angle. A number of other lines in the region of 20509 cm^{-1} may be assigned to a combination of uranium-ligand stretching vibrations with lattice vibrations ω.

The search in the absorption spectrum for the vibration ν_3 of the uranyl ion is somewhat difficult, since the corresponding spectral region (20868 cm^{-1}) coincides with the line ν_2 of UO_2^{2+} for the second electronic transition. The vibration ν_3 in the luminescence spectrum is polarized perpendicular to the b.o.u.; consequently, the corresponding line in the absorption spectrum should have the same polarization. If the line $\nu = 20868$ cm^{-1} corresponds to an electronic-vibrational transition associated with excitation of the antisymmetric vibration of the uranyl ion, then the difference $\nu - \nu_0$ will be equal to 776 cm^{-1}. The analogous vibration in the luminescence spectrum at this same temperature has a frequency of 913 cm^{-1}. The ratio of the frequencies of the antisymmetric and totally symmetric vibrations ν_3/ν_1 in the lower and upper excited states will be 1.109 and 1.112, respectively, which agrees within 1-2%. Additional confirmation of the indicated assignment is the isotope shift of the 20868 cm^{-1} line, observed in (9), upon replacement of U^{238} by U^{235}. The decrease in the frequencies of the stretching vibrations of the uranyl ion in the excited state occurs as a result of weakening of the uranium-oxygen bond.

In the region of 20635 cm^{-1} in the absorption spectrum, a sharply polarized line is observed, which should be assigned to the 0—0 transition of the second excited electronic state. It gives rise to the development of a new series of lines, repeated with a frequency of 710 cm^{-1}, ν_1 of the uranyl ion of the second electronic transition. Here one should note the active vibration 190 cm^{-1}, which has the same polarization as the frequency of the purely electronic transition. The lines,

Table 1

Frequencies (in cm^{-1}) of the luminescence and absorption spectra of the cesium uranyl chloride crystal at 77° K

Luminescence	Absorption I	Absorption II	Absorption III	Absorption IV	Assignment
20092	20092	20635	22625	26189	ν_0 purely electronic transition
21					
42					
80					
114 *	110 *		115	102 *	ω_1
				108 *	
	204 *	190 *	177 *	165 *	ω_2
				173 *	
243 *	233 *	235 *	230 *	231 *	ν_{U-L}
261 *	247 *	243			$\nu_2 UO_2^{2+}$
289 *	274 *		279 *	281 *	$\nu_2 UO_2^{2+}$

Luminescence	Absorption I	Absorption II	Absorption III	Absorption IV	Assignment
324 *	313		300 *	302 *	$\nu_{\mathrm{U-L}}$
			319 *		
	345 *	340 *	337		$\nu_2 \mathrm{UO}_2^{2+} + \omega_1$
379	371 *			360	$\nu_2 \mathrm{UO}_2^{2+} + \omega_1$
445	413	409			$\nu_{\mathrm{U-L}} + \omega_1$
	425				
476					$2\nu_{\mathrm{U-L}}$
510	512		503		$2\nu_2 \mathrm{UO}_2^{2+}$
	524		548		
			610 *	640 *	$2\nu_{\mathrm{U-L}}$
832 *	716 *	710 *	719 *	725 *	$\nu_1 \mathrm{UO}_2^{2+}$
913 *	776 *	772 *	758 *	784 *	$\nu_3 \mathrm{UO}_2^{2+}$

corresponding to the vibrations 235, 243, and 409 cm^{-1}, are very weak. The activation of some vibrations and the weakening or disappearance of others indicate a change in the symmetry of the molecule upon its transition to the next excited state. It is possible to record the repetition of the totally symmetric valence vibrations of the uranyl ion in the second electronic transition up to 4—5 quanta.

The overlap of the first and second excited electronic states leads to a complication of the absorption spectrum in both components. In component 2, in the region of the second overtone of the totally symmetric valence vibrations of the uranyl ion, two lines, 22237 and 22290 cm^{-1}, are observed, with an interval of 53 cm^{-1}. In the short-wavelength region of the spectrum (23660 cm^{-1}) four lines can be detected: 23646, 23663, 23694, and 23711 cm^{-1}. The magnitude of the frequency difference between the first and second, third and fourth lines is 17 cm^{-1}, and between the first and third it is 48 cm^{-1}. If their appearance is considered to be the result of splitting of the totally symmetric valence vibration of the uranyl ion, then the nature of this splitting is presently unclear.

Further, upon moving into the ultraviolet region of the absorption spectrum, we find a new series of lines that cannot be correlated with the first and second considered above. This series of lines should be assigned to the third excited electronic state. The periodicity of the lines of this series (719 cm^{-1}) is repeated up to 6—7 quanta of totally symmetric

of stretching vibrations of the uranyl ion. It is necessary to note, for this series, the active vibrational frequency of 319 cm^{-1}.

In the near ultraviolet one more series of lines is observed, which, on the basis of the magnitudes of the absorption coefficients and the polarization of individual lines, should be assigned to the fourth electronically excited state. Its beginning coincides with the line 26189 cm^{-1}, which belongs to a purely electronic transition polarized parallel to the optical axis.

The vibrations 110 and 170 cm^{-1} appear as doublets polarized in different directions, with a splitting magnitude of 6–8 cm^{-1}. The most active vibration is 231 cm^{-1}, with polarization perpendicular to the optical axis. The periodicity of the lines of this series is 725 cm^{-1}, and their repetition can be recorded up to 2–3 quanta of the totally symmetric stretching vibrations of the uranyl ion, after which a sharp increase in the absorption coefficient and the disappearance of the structure occur.

Thus, analysis of the polarization of the lines and of the spectral intervals between them in the absorption spectrum of the crystal $CsUO_2Cl_4$ at 77°K makes it possible to distinguish, in the structured region, four excited electron-vibrational states with substantially different characteristics.

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REFERENCES

1. S. P. McGlynn, J. K. Smith, *J. Mol. Spectroscopy*, **6**, 164 (1961).
2. K. V. Narasimham, *Develop. Appl. Spectry*, **2**, 142 (1962).
3. D. D. Pant, *Proc. Indian Acad. Sci.*, **31A**, 35 (1950).
4. A. I. Komyak, A. N. Sevchenko, E. V. Ditsh, *Dokl. AN BSSR*, **12**, No. 9 (1968).
5. A. I. Komyak, A. N. Sevchenko, *Dokl. AN BSSR*, **12**, No. 12 (1968).
6. A. I. Komyak, L. V. Volodko, *Izv. AN BSSR, ser. fiz.-matem. nauk*, No. 1 (1969).
7. L. V. Volodko, A. I. Komyak, L. E. Slepov, *Zhurn. prikl. spektroskopii*, **3**, issue 2, 134 (1965).
8. L. V. Volodko, A. I. Komyak et al., *Izv. AN SSSR, ser. fiz.*, **32**, No. 8, 1394 (1968).

9. G. N. Dicke, A. B. F. Dunkan, *Spectroscopic Properties of Uranium Compounds*, N. Y., 1949.

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