ISOTOPIC EFFECT IN THE FLUORESCENCE SPECTRA OF AMMONIUM URANYL SALTS

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Abstract

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ISOTOPIC EFFECT IN THE FLUORESCENCE SPECTRA OF AMMONIUM URANYL SALTS

A characteristic feature of the absorption and luminescence spectra of uranyl compounds in the solid phase at $T < 100^{\circ}$ K is the presence of fine structure ([1]). As the decisive factor determining its appearance, it was proposed to regard the crystal lattice, which, together with the uranyl group, forms the electronic-vibrational spectrum ([2,3]). The accumulation of experimental material made it possible to make the concept of the crystal lattice more concrete and to relate the spectrum to the real structure of the molecule. As a result of investigation of the spectral-luminescent characteristics of a large number of simple salts and complex uranyl compounds, with the use of results of theoretical calculation, the spectra were found to contain the frequencies of intramolecular vibrations of all the constituent parts of uranyl compounds (anions, cations, neutral ligands, etc.) ([4]). The basis for the interpretation was the coincidence of frequency intervals in the luminescence spectra and of the corresponding values of bands in the infrared absorption spectra. To confirm such an assignment, in a number of cases the isotopic effect was used ([1,5–7]). Thus, on the basis of the displacement of lines in the luminescence spectrum of cesium uranyl nitrate when atoms of N^{14} were replaced by the isotope N^{15}, the presence of nitrate-ion vibration frequencies was established with sufficient reliability ([1]).

Another example concerning the manifestation of vibration frequencies of neutral ligands may be the significant change in the luminescence spectra of hydrates of uranyl salts when hydrogen is replaced by deuterium in the molecules of crystallization water ([6,7]). As for the observation in the luminescence spectra of double uranyl salts of the vibrational frequencies of complex cations, all authors, in assigning them, rely only on intuition ([8]). Without entering here into a discussion of the questions of the uniqueness and reliability of such a criterion of interpretation, it should nevertheless be emphasized that the reliability of the manifestation of intramolecular vibrations of cations in fluorescence spectra can be confirmed only by isotopic replacement of individual atoms in these groups.

In the present work we present the results of spectroscopic investigations of the compounds $(NH_4)_2UO_2(SO_4)_2 \cdot 2H_2O$ and $(NH_4)_2UO_2Cl_4 \cdot 2H_2O$ upon replace-

ment of N^{14} atoms by N^{15}, which were obtained by known methods ([9–11]) from the starting $(NH_4)_2SO_4$ and NH_4Cl, enriched with the heavy isotope to 93 and 91%, respectively. Their composition was checked by spectral methods; elemental analysis was also carried out. Luminescence was recorded at the temperature of liquid nitrogen with an ISP-67 spectrograph (camera with $f = 1500$ mm) over a broad exposure range on "Izopanchrom-250" photographic plates. Infrared absorption spectra were recorded on a UR-10 spectrophotometer. The samples were pressed in KBr pellets or ground in vaseline oil (KBr windows) and in fluorinated kerosene (CaF_2 windows).

In the free state, the complex cation NH_4^+ belongs to the point symmetry group T_d. In infrared and Raman spectra it is characterized by four different vibration frequencies: fully–

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Fig. 2. Luminescence spectra of $(NH_4)_2UO_2Cl_4 \cdot 2H_2O$ (**I**) and $(NH_4)_2UO_2(SO_4)_2 \cdot 2H_2O$ (**II**):
a –spectra of samples with N^{14}; *b* –spectra of samples with the isotope N^{15}. Arrows indicate the lines for which an isotopic shift was found.

symmetric stretching ν_1, doubly degenerate deformation ν_2, triply degenerate antisymmetric stretching ν_3, and triply degenerate deformation ν_4. Of these, in IR absorption usually only ν_3 and ν_4 are active, their regions of manifestation being ~ 3140 and ~ 1400 cm^{-1}, respectively ([12]). When chemical bonds are formed in complex crystalline compounds, the symmetry of the NH_4^+ cation is lowered, which may lead to removal of the prohibition for ν_1 and ν_2 and to splitting of the degenerate frequencies. An example of this is the vibrational spectrum of crystalline NH_4NO_3, in which all four frequencies are active ([13]).

Figure 1 gives the IR spectra of $(NH_4)_2UO_2Cl_4 \cdot 2H_2O$ *(I)* and $(NH_4)_2UO_2(SO_4)_2 \cdot 2H_2O$ *(II)*. As is seen from the figure, the spectra *I* and *II* show the frequencies of all the constituent parts of the complexes UO_2^{2+}, SO_4^{2-}, NH_4^+, H_2O. At the same time, the isotopic shift upon replacement of N^{14} by N^{15} is noticeable in both cases only for the band lying at ~ 1400 cm^{-1}. The shift of the position from 1427 to 1410 cm^{-1} (for $(NH_4)_2UO_2Cl_4 \cdot 2H_2O$) and from 1435 to 1422 cm^{-1} (for $(NH_4)_2UO_2(SO_4)_2 \cdot 2H_2O$) confirms the correctness of assigning it to the deformation vibration N–H. In the region of stretching vibrations N–H, the broad absorption bands of medium intensity are masked by the strong absorption of the stretching vibrations of water OH, which makes reliable detection of an isotopic effect on them difficult.

Fig. 1. IR absorption spectra of $(NH_4)_2UO_2Cl_4 \cdot 2H_2O$ *(I)* and $(NH_4)_2UO_2(SO_4)_2 \cdot 2H_2O$ *(II)*. Asterisks denote bands in the spectra of samples with the isotope N^{15}.

In the luminescence spectra of the same substances a large number of sufficiently narrow lines is observed (Fig. 2), which makes it possible to determine even small changes in their position upon isotopic substitution and makes the

Fig. 1. IR absorption spectra of (NH4)2UO2Cl4 · 2H2O (I) and (NH4)2UO2(SO4)2 · 2H2O (II). Asterisks denote bands in the spectra of samples with the N15 isotope.

Figure 1: Fig. 1. IR absorption spectra of (NH4)2UO2Cl4 · 2H2O (I) and (NH4)2UO2(SO4)2 · 2H2O (II). Asterisks denote bands in the spectra of samples with the N15 isotope.

luminescence method more sensitive in comparison with IR absorption. Thus, for $(NH_4)_2UO_2(SO_4)_2 \cdot 2H_2O$ a shift of ~ 7 cm^{-1} is clearly noticeable for the line separated from the purely electronic transition by 1431 cm^{-1} toward the low-frequency region. It is regularly repeated in the second, third, fourth, and fifth bands. This makes it possible to assign the last frequency to the deformation vibration N—H. A shift of any other lines for this compound was not detected. In the luminescence spectrum of $(NH_4)_2UO_2Cl_4 \cdot 2H_2O$, in the region of the N—H stretching vibrations, a shift is noticeable for the line separated from the purely electronic transition by 3268 cm^{-1}. It falls in the fourth band of the spectrum, and for it there are no homologues in the preceding region. The magnitude of the shift is ~ 6 cm^{-1} and lies at the limit of experimental accuracy for this spectral region; however, the very fact of the shift has been established quite reliably by repeated measurements. This character of the behavior of the spectral line under consideration upon replacement of N^{14} by N^{15} makes it possible to assign it to the optical transition to the level of the N—H stretching vibration. The fact that in the luminescence spectrum of $(NH_4)_2UO_2(SO_4)_2 \cdot 2H_2O$ deformation vibrations N—H were found and stretching vibrations N—H were not found, whereas in the spectrum of $(NH_4)_2UO_2Cl_4 \cdot 2H_2O$, on the contrary, stretching vibrations are present and deformation vibrations N—H do not appear, can be explained by a difference in the structure and symmetry of these two compounds ([14,15]) (Fig. 2, see insert facing p. 1263).

Upon replacement of N^{14} by N^{15} in $(NH_4)_2UO_2Cl_4 \cdot 2H_2O$, significant changes are observed in the first band of the fluorescence spectrum. At a distance of 150-170 cm^{-1} from the purely electronic transition, two lines appear: a narrow one at 156 cm^{-1} and a broad one at ~ 165 cm^{-1}. Isotopic substitution shifts the second line by ~ 7 cm^{-1} into the low-frequency region and leads to its partial overlap with the first, which unequivocally proves its ammonium origin. The low value of the frequency (~ 165 cm^{-1}) can apparently be explained by the fact that it most likely corresponds to vibrations of the NH_4^+ group as a whole with respect to the complex uranyl ion. These polyatomic groups are bound by ionic forces and have large oscillating masses.

Thus, as a result of a spectroscopic study of the double uranyl salts $(NH_4)_2UO_2Cl_4 \cdot 2H_2O$ and $(NH_4)_2UO_2(SO_4)_2 \cdot 2H_2O$ under isotopic replacement of N^{14} atoms by N^{15} atoms, three different types of vibrations of the NH_4^+ cation were identified. Taking into account the low probability of transfer of vibrational energy between the central ion UO_2^{2+} and the outer-sphere particle

NH_4^+ according to the laws of elastic forces, the fact that the frequencies of vibrations of the NH_4^+ group appear in the luminescence spectra of uranyl compounds can be explained if one assumes the existence of intramolecular energy exchange due to collectivization of the electron shells of the individual constituent parts of the complex.

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Note: Figure translations are in progress. See original paper for figures.