

Direct observation of strong-electron orbit hybridization in the internal-conversion electron spectra

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The differential spectrum of the conversion electrons of uranium 235 trioxide ($1/2^+$) isomer and the x-ray electron spectrum of γ - UO_3 in the 0 to 40-eV range of electron binding energy were measured. An experimental proof of appreciable hybridization with respect to the deep 2s orbits of oxygen and fluorine with 6p orbits of the uranium atom in the solid-phase compounds γ - UO_3 and UF_4 , respectively, was obtained.

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It is known that the radioactive decay constant, including isomeric transitions, depends on the chemical environment of the radioactive atom. Despite the fact that the changes in the decay constant are small, the existence of these effects has been reliably established and widely discussed.¹⁻⁴

Our investigation involves the study of the effect on chemical environment on the structure of the spectrum of internal-conversion electrons of low-energy nuclear transitions. It seems to us that these data can yield much more complete information about the nature of the chemical bond than measurements of the radioactive decay constant.

As a result, investigation of the conversion spectrum of the chemical compounds

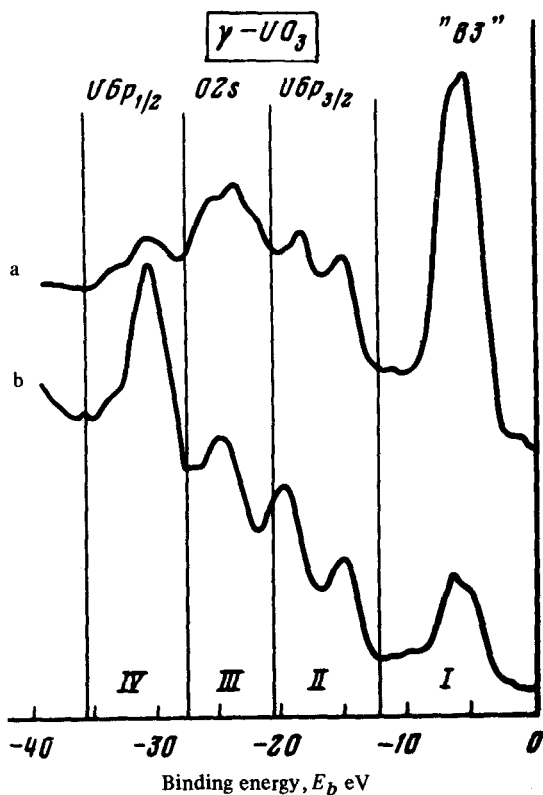


FIG. 1. Comparison of x-ray electron (a) and conversion (b) spectra of uranium trioxide.

of uranium-235 isomer with a transition energy⁵ of 76.8 eV, for which the observed variations of the decay constant amount to a few percent, are of special interest.

Previously we had investigated the conversion electron spectrum for uranium tetrafluoride, in which the uranium nucleus is in an excited state.⁵ In this paper we investigate the γ - UO_3 compound.

The uranium trioxide was synthesized using the standard method described in Ref. 6. The chemical composition of the compound was checked by x-ray electron spectroscopy method.⁷ The original samples for isomer implantation were prepared by embedding the γ - UO_3 powder in indium deposited as a thin layer on a gold substrate. The isomer was inserted into the γ - UO_3 during electrostatic collection, in an atmosphere of spectrally pure oxygen, of the $^{235\text{m}}\text{U}$ recoil atoms produced in the α decay of ^{239}Pu .⁵

The activity of the working samples was $\sim 10^5$ decays/sec.

The spectra were measured using an HP 5950A ESCA electrostatic electron spectrometer. The characteristics of the spectrometer and its calibration procedure are indicated in Ref. 5. Like in our previous work, the identification of the conversion-spectrum lines and determination of the electron binding energy corresponding to

them were done by comparing the conversion and x-ray electron spectra of the same chemical compound. The C 1s line of sorbed carbon, whose location corresponded to 285.0 eV on the spectrometer scale, served as the reference point for reading the electron binding energy.

Figure 1 shows the x-ray electron (a) and conversion (b) spectra of γ -UO₃ in the electron binding energy region of 0 to 40 eV. A comparison of these spectra shows that they are in good agreement. The x-ray electron spectrum is similar to the uranium trioxide spectrum given in Ref. 7.

At the same time, a comparison of the uranium isomer spectra in the trioxide and tetrafluoride case reveals a drastic difference in their structure. Three maxima were observed in the UF₄ conversion spectrum⁵ and five maxima in the γ -UO₃ spectrum (Fig. 1b). This difference in the structure of conversion spectra can be accounted for only by the different chemical environment of the ^{235m}U in these compounds.

Further, let us isolate four region (on the electron binding energy scale) in order to discuss the structure of the observed x-ray, electron, and conversion spectra: I (0–12 eV), II (12–21 eV), III (21–27 eV), and IV (27–35 eV). We attribute region I to the "intrinsic valence band" (VB) of uranium trioxide; the 6p_{3/2} orbit of the free uranium atoms lies in region II; the 2s orbit of the free oxygen atom lies in region III; the 6p_{1/2} orbit of uranium lies in region IV.

An earlier calculation⁴ of the conversion probability $w(E3[nlj])^1$ per electron in the population of the (nlj) orbit of a free uranium atom with the recommended shell configuration

$$R_n [6s_{1/2}]^2 [6p_{1/2}]^2 [6p_{3/2}]^4 [6d]^1 [5f]^3 [7s]^2$$

showed that the conversion process is strongest in the (6p_j) and 6d_j orbits, where the conversion probability in the (6d) orbits is an order of magnitude less than that in the (6p) orbits, and the contribution of the (7s) and (5f) orbits can be ignored.

The strong peak in region I of the γ -UO₃ conversion spectrum (like in the UF₄ case) is attributable only to hybridization of the electron orbits in the molecule, so that there is an appreciable admixture of the p orbit of a uranium atom in the components of the wave functions of these orbits. The calculations for the UF₆ compound⁸ in the literature favor this picture. An alternative explanation requires the assumption of a radial (several fold) increase in the fraction of the d orbit of a uranium atom in the molecular orbits that lie in this band of the spectrum.

An agreement of the conversion and x-ray electron spectra in regions II and IV is understandable, since the 6p_{3/2} and 6p_{1/2} orbits in the free uranium atom, in which the conversion process proceeds intensively, belong to these regions of the spectrum.

The peak in region III of the conversion spectrum, which contains the 2s orbit of the free oxygen atom, is the most dramatic feature of the spectrum, illustrating the extent to which the atoms of the nearest chemical environment of the isomer influence the conversion process.

Since the electromagnetic field of the 76.8-eV nuclear transition is characterized by the wavelength $\lambda \sim 26\text{\AA}$, which is considerably greater than the interatomic distances in the molecule or condensed medium, we can assume that the line in region III

corresponds to the conversion of the $E 3$ multipole in the electron shells of the neighboring oxygen atoms that surround the uranium atom. However, our calculations showed that the conversion probability of the electrons of the neighboring atoms in the case of uranium-235 isomer does not exceed 10^{-6} of the conversion probability for electrons in the neighborhood of the excited nucleus. The point is that within an accuracy better than 1% the internal conversion process of the $E 3$ multipole of uranium with an excitation energy of 76.8 eV is concentrated within a 0.05-Å radius of the isomer nucleus.

Thus, the strong peak in the spectrum with an energy of ~ 25 eV, which is close to that of the $2s$ electrons of an oxygen atom, can be accounted for only by appreciable hybridization of these orbits with the $6p$ energy-proximate orbits of uranium in which the internal conversion process is intensive.

We can understand within the context of this picture the complex structure of the peak in the conversion spectrum of the uranium tetrafluoride isomer⁵ with a binding energy of ~ 35 eV, which can be accounted for by appreciable hybridization of the $2s$ orbit of fluorine and the $6p_{1/2}$ orbit of uranium, whose binding energies almost coincide.

Investigation of the conversion spectra of uranium trioxide and tetrafluoride isomer made it possible to determine experimentally the molecular orbitals with a noticeable fraction of the p orbit of a uranium atom up to a binding energy of ~ 40 eV.

We assume that study of the conversion spectra of low-energy nuclear transitions (to 10 keV) in combination with calculation of the internal conversion probability is an effective method of determining the chemical binding. This method provides a unique possibility of determining the hybridization of relatively deep electron orbits.

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