Quantitative conversion spectroscopy of the ultrasoft isomeric transition of uranium-235 and the electronic structure of uranium oxides

A. D. Panov

Russian Scientific Center "Kurchatov Institute," 123182 Moscow, Russia

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Combined measurements of conversion electron spectra and the decay constant (76.5 eV, $(1/2)^+ \rightarrow (7/2)^-$) of the $E3$-isomeric transition of the uranium-235 nucleus have been performed with collection of the isomer atoms on an indium surface. The conversion spectra are interpreted as corresponding to a mixture of two different oxides A and B of uranium, one of which (A) is similar to UO_2, and the other (B) consists of a uranium–oxygen cluster based on the linear uranyl group O–U–O. From a set of mixed experimental spectra conversion spectra have been found corresponding to the chemical states A and B of the isomer atoms, and the variation of the absolute intensities of the conversion lines has been quantitatively investigated for them by varying the chemical composition of the isomer atoms and the ratio between the intensities of various conversion lines of the B spectrum. Experimental ratios between the intensities of the conversion lines are compared with the expected ratios in accordance with the distribution of the $6p$ electron density in the uranyl group. It is concluded that the experimental data agree with the calculation and that abrupt violations of proportionality of the partial probabilities of conversion of the electron density near the nucleus are absent. In accordance with the hypothesis of proportionality of the partial probabilities of conversion, an experimental estimate is given of the degree of localization of the deep-lying uranium $6p_{1/2}$ shell during formation of the chemical bond in the uranyl group: around 70% of the $6p_{1/2}$ electron density remains in the quasi-atomic uranium shell and around 30% is transferred to hybrid molecular orbitals.
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1. INTRODUCTION

As theoretical and experimental studies have shown, the internal conversion electron spectra of nuclear reactions can be extraordinarily informative about the electronic structure of matter if an energy resolution on the order of 1 eV is achieved in such spectra. A study of variations of the shape of the conversion spectrum associated with a change in the chemical environment of the converting atom would be of special interest. High-resolution conversion spectroscopy, used to investigate the electronic structure of matter, has acquired the name conversion electron spectroscopy.[1] However, as a consequence of a number of experimental difficulties it appears that so far it has been possible to extend the technique of conversion electron spectroscopy only to the soft conversion transitions of five nuclei: ^{235}U, ^{99}Tc [see references in Ref. 1 (review)], ^{119}Sn, ^{73}Ge (Ref. 2), and ^{201}Hg (Ref. 3). The ultrasoft isomeric transition of the ^{235}U nucleus occupies a special place among these objects.

The ^{235}U nucleus has the excited state $(1/2)^+$ (Refs. 4 and 5), whose energy according to the most recent data is only 76.5±0.4 eV (Ref. 6). This is a long-lived isomeric state (^{235m}U), and decay of the nucleus to the ground state $(7/2)^-$ is realized via the almost completely converted $E3$ transition (conversion coefficient $\sim 10^{21}$, Ref. 7) with half-life around 26 min.[4,5] The conversion process is energetically resolved for the filled subshells $(6s_{1/2})^2$, $(6p_{1/2})^2$, $(6p_{3/2})^4$, and for the valence electrons of the uranium atom.

The isomeric transition of ^{235m}U is the softest of the nuclear transitions that can be reliably observed at present; therefore, the conversion process of this transition possesses a number of unique properties (e.g., the possibility of manifesting strong interference effects, see below). Only one case is known in which the nuclear excitation energy is less than for ^{235m}U, and that is ^{229m}Th with an excitation energy of 3.5±1.0 eV (Ref. 8); however, there are still no direct experimental observations of the decay of this isomer, and its decay mechanism is unknown. All other known nuclear transitions, which, in principle, can be observed by conversion spectroscopy, have energies not less than 1 keV (Ref. 1). Let us touch on the nature of the low-lying $(1/2)^+$ state of the ^{235}U nucleus.

The ^{235}U nucleus is a strongly deformed ($\delta \approx 0.25$, Ref. 9, p. 125) odd nucleus. The lower energy diagram of this nucleus is qualitatively well interpreted as a set of rotation bands based on single-particle states of the unpaired nucleon in the self-consistent field of the deformed even core (Ref. 9, Ch. 5, Sec. II). In a spherically symmetric potential the characteristic separations between the single-particle levels are on the order of 1 MeV with degeneracy in the magnetic quantum number m_j. For violation of spherical symmetry the degeneracy in m_j is removed, and each state splits into several sublevels, with the magnitude of the splitting rapidly growing with growth of the deformation of the potential. Starting with deformations $\delta \sim 0.1$, the sublevels belonging to various initial (nlj)-subshells of the spherically symmetric potential begin to intersect; hence the possibility arises of forming very closely situated single-particle states.

The $(7/2)^-$ ground state of the ^{235}U nucleus and the isomeric state $(1/2)^+$ according to the experimental data of Ref. 10 are interpreted as the initial states of rotational bands constructed, respectively, on the $[743]\frac{7}{2}^-$ and $[631]\frac{1}{2}^+$ orbitals of the neutron in the field of the even core of ^{234}U. Therefore, it may be surmised that the proximity of the $(7/2)^-$ and $(1/2)^+$ states of uranium-235 is explained by an overlap of the magnetic sublevels of the various initial (nlj)-shells of the spherically symmetric potential. This assumption is confirmed by calculations of single-particle states of the neutron in the Nilson[11] and Saxon–Woods[12] potentials, which are qualitatively similar. According to these calculations, the $[743]\frac{7}{2}^-$ and $[631]\frac{1}{2}^+$ states are associated, respectively, with the $1j_{15/2}$ and $3d_{5/2}$ states of the initial spherically symmetric potential. In the spherically symmetric potential the $1j_{15/2}$ and $3d_{5/2}$ states are separated in energy by more than 1 MeV. However, for deformations $\delta = 0.2 - 0.4$ the sublevels $[743]\frac{7}{2}^-$ and $[631]\frac{1}{2}^+$ approach each other and almost overlap. Herein lies the qualitative explanation of the proximity of the $(7/2)^-$ and $(1/2)^+$ states. Indeed, the picture is somewhat more complicated, since these states are purely single-particle states—they may contain a noticeable admixture of collective excitations.[12,13]

The principles of the experimental technique of conversion electron spectroscopy applied to ^{235m}U conversion were laid down in Ref. 14, and in Ref. 15 results were obtained by means of a new technique which are very important for the theory of the chemical bond of heavy elements (formation of inner valence molecular orbitals—molecular orbitals with the participation of deep, completely filled atomic shells) but which are of a qualitative character. It would be of extreme interest to make the transition to quantitative studies of the electronic structure of uranium compounds using conversion electron spectroscopy, and this is the main aim of the present paper.

To refine the statement of the problem, it is necessary to say a few words about the correspondence between current theory and experiment in the conversion spectroscopy of the uranium-235 isomer. Ground-breaking works in the theory of conversion of the uranium isomer are those of Grechukhin and Soldatov.[13,16] First of all, these papers established the abrupt difference in probability of conversion of the $6p_{1/2}$ and $6p_{3/2}$ electrons of uranium (binding energy, respectively, around 30 eV and 20 eV, Ref. 17). Second, they investigated the not entirely trivial question of spatial localization of the conversion process of ^{235m}U. The degree of localization of the transition is determined by the rate of convergence of integrals of the form $\langle f|r^{-4}|i\rangle$ (Refs. 13 and 16) as a function of the radius R of the region of integration. Here $|i\rangle$ is the initial state of the electron in an atomic orbit and $|f\rangle$ is its final state in the continuum. In Ref. 16 it was shown in numerical calculations that for the $6p$ and $6d$ electrons of uranium, integrals of this type converge to within 1% of their total value within a region of radius $0.1a_0$, where a_0 is the Bohr radius. A sphere of radius $0.1a_0$ may be taken as the region of localization of the conversion process of ^{235m}U. And finally, for the case of conversion in a single uranium atom it was shown that with very high accuracy (better than 1%) the partial probabilities of conversion on the $6p_{1/2}$ and $6p_{3/2}$ electrons of uranium are proportional to the square of the corresponding wave functions at the nucleus and depend on neither the binding energy[13] nor the configuration of valence shells of the atom.[16] It is specifically this property of the conversion spectrum of the uranium-235 isomer that is important for investigating the electronic structure of matter. Estimates have been given using the approach developed in Refs. 13, 16, and 18 of possible chemical variations of the decay constant of the uranium isomer. Variations of the decay constant of the uranium isomer were studied experimentally in Refs. 19–25. The scale of chemical variations of the decay constant observed in these studies (3–5%) is somewhat smaller than the maximum possible variations of the decay constant theoretically predicted.[13,16,18] This might have been expected since quite exotic configurations of the electronic shell of the uranium atom were considered, which apparently are not realized in experiment. In other respects it may be stated that at this stage experiment is in reasonable agreement with theory.

References 13 and 16 did not take into account variations in the amplitudes of the continuum states of the conversion electron in the conversion zone due to elastic scattering of the electron by atoms of its environment and subsequent interference. This effect was considered in a paper by Dobretsov.[26] Instead of the small corrections to the conversion probability which might have been expected, in a number of cases the interference effect turns out to be quite large. Thus, according to Ref. 26, in the conversion of the uranium isomer in the atomic cluster UAg_{12} corrections to the partial probabilities of conversion on individual atomic orbitals reach 89% of their unperturbed values, and the value and sign of the correction oscillate with variation of the energy of the orbital and with variation of the distance to the atoms of the environment. In this case the direct connection between the line intensities of the conversion spectrum and the electron densities at the nucleus established earlier in Refs. 13 and 16 is completely lost.

However, the results of Ref. 26 apparently do not completely agree with the experimental facts. Indeed, although Ref. 26 deals only with decay of the uranium isomer in an environment of silver atoms, the predicted interference effect should undoubtedly also manifest itself in many other cases. It should lead to characteristic variations of the decay constant of the uranium isomer on a scale of 20% or even greater (up to 47%, Ref. 26), which significantly exceeds the values observed in experiment. The experimentally observed variations of the decay constant most likely have a purely chemical magnitude, and interference effects apparently do not manifest themselves in any way.

It should be noted, however, that variations of the decay constant in the given case are not a very good test of the theory. The possibility cannot be excluded that interference gives large contributions to the partial probabilities of conversion belonging to individual atomic orbitals where these contributions have opposite sign and mutually cancel so that the decay constant varies only slightly. Observations of the chemical variations of the intensities of separate lines of the conversion spectrum would give much more detailed data.

These considerations lead to the following refinement of the formulation of the problem of the present work. First of all, it is necessary to develop a technique that would allow one to experimentally measure the absolute values of the partial probabilities of conversion belonging to individual atomic or molecular orbitals or ratios of these probabilities. The quantities obtained with the help of the new experimental technique could then be compared with the expected electron density distribution on the uranium nucleus or with chemical variations of the electron density in order to elucidate to what extent the experimental data support proportionality between the partial probabilities of conversion and the electron densities.[13,16] If indications upholding such a proportionality are obtained, then we must explain why the interference effects predicted in Ref. 26 not show up in experiment. Finally, if an understanding is reached here, then conversion spectroscopy of the uranium isomer may be used in practice to investigate the electron density distribution in uranium-containing molecules and clusters.

2. EXPERIMENTAL TECHNIQUE AND SAMPLES

To prepare samples containing the ^{235m}U isomer, the technique developed in Refs. 14 and 15 is used in the present work with minor modifications and additions. The ^{235m}U isomer was obtained as the product of α decay of ^{239}Pu in $^{239}PuO_2$ deposited as a thin layer ($\sim 20\ \mu m/cm^2$) on the inner surface of a platinum hemisphere of radius 40 mm (Ref. 27). The ^{235m}U recoil atoms were collected by an electric field onto metal substrates placed near the center of the hemisphere. All experimental results presented in this paper were obtained by collecting the isomer in an air atmosphere at a pressure of 70 GPa. It was found that the composition of the gaseous medium in the accumulation chamber only weakly affects the chemical state of the isomer atoms in the samples, as may be assessed from the form of the measured conversion spectra. The working region of the sample was bounded by a teflon mask with a rectangular opening with dimensions $0.5\times 5\ mm^2$. The typical collection time of an isomer atom was 40 min, and the discharge current could be regulated within the limits 1–5 nA. The potential difference between the sample and the plutonium hemisphere was around 1 kV (minus on the sample). The composition of the surfaces of the samples after isomer collection was monitored by x-ray electron spectroscopy and by α-activation of ^{239}Pu. Contamination of the surface by plutonium or teflon decomposition products was not observed. The total activity of the sample immediately after termination of isomer collection was usually on the order of 10^5 uranium isomer conversion decays per second. The samples were transferred in air to the electron spectrometer after unsealing of the accumulation chamber.

In the collection of uranium isomer onto the surface of a metallic sample the isomer atoms do not at first reach the metal surface, but first reach the film of hydrocarbon contaminants sorbed in the metal surface. The characteristics of the hydrocarbon film for copper substrates which have been taken through a typical cycle of uranium isomer collection were examined in Ref. 28 by x-ray electron spectroscopy. The film thickness amounts to around 15 Å, the total atomic density of oxygen and carbon is roughly equal to the atomic density of copper, i.e., $8.5\times 10^{22}\ cm^{-3}$, and the carbon and oxygen atoms are present in different concentrations (within the limits of statistical error). The uranium isomer atoms succeed in braking completely in the hydrocarbon film, where with a probability of nearly 100% they bind with oxygen.[29]

To measure the conversion spectra of ^{235m}U we used a production-model NR5950A electron spectrometer[30] with a pre-acceleration system built by the authors of Ref. 14. The nominal working energy range of the spectrometer is 300–1500 eV. Analysis of the electron energies is properly performed with the help of a spherical electrostatic analyzer (180°) having a constant potential difference between the electrodes. The measurements are performed simultaneously over an energy interval approximately 10 eV in width located near 115 eV. Before entering the spherical analyzer, the electrons are focused and braked to the necessary energy with the help of a preparatory electron-optical system consisting of four electron lenses. If it is required to measure a spectral interval wider than 10 eV, then the spectrum is scanned by varying the braking potential. In order to fit the uranium isomer conversion spectrum (which extends from 0 to roughly 75 eV) into the working range of the spectrometer, an accelerating voltage of -500 eV relative to the entrance to the first (grounded) electron lens of the preparatory electron-optical system is applied to the sample. The samples are placed in the spectrometer chamber, which has a working vacuum on the order of 10^{-9} Torr, through a transfer drawer with differential evacuation. The procedure of placing a sample in the spectrometer takes 1–2 min. The conversion spectra were measured in energy intervals of 20 and 50 eV and written to the 256-channel analyzer of the spectrometer. The energy resolution of the spectrometer is better than 1 eV (Ref. 14) and does not depend on the electron energy. The procedure of energy calibration of the conversion spectra is described in Sec. 4.

3. QUANTITATIVE ANALYSIS OF CONVERSION SPECTRA OF URANIUM-235

Figure 1 displays two experimental uranium-isomer conversion spectra measured with the help of the NR5950A spectrometer that are typical for uranium-isomer collection onto metal substrate surfaces. An obstacle to correct analysis of the spectra is presented by two types of distortions of the shape of the initial conversion spectrum. The first type of distortion is associated with inelastic scattering of the conversion electrons in the sample. Each conversion peak generates a low-energy tail consisting of inelastically scattered and secondary electrons. By adding together, these tails create an intense background of complex shape on which the conversion peaks are imposed (Fig. 1). Another distorting factor consists of instrument effects, the main one of which is the dependence of the effective geometrical factor of the spectrometer on the electron energy (variability of the spectrometer transmission function). Thus, mathematical processing of the spectra should consist first of correction of the experimental spectra for inconstancy of the spectrometer transmission function, then of subtracting out the inelastic

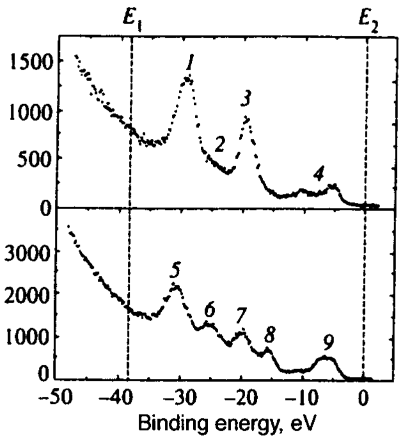

FIG. 1. Experimental conversion spectra of the uranium isomer for isomer collection on an indium surface. The spectra differ in the chemical state of the isomer (see Sec. 4) and correspond approximately to the extreme possibilities realized in experiment. The binding energy of the electrons corresponding to the conversion peaks is plotted along the abscissa; the kinetic energy increases from left to right. (E_1,E_2) is the informative spectral interval. The labels on the lines in the figure are as follows: 1—"$6p_{1/2}$," 2—"O2s," 3—"$6p_{3/2}$," 4—VB, 5—"$6p_{1/2}$," 6—"O2s," 7—"$6p_{3/2}(l)$," 8—"$6p_{3/2}(r)$," 9—VB.

background, and finally in determining the areas (which we also call intensities) of the widths1) and positions of the lines. The latter problem is solved here by decomposing the spectra into lines of Gaussian shape by using the maximum likelihood method. The adequacy of the decomposition was monitored by the quantity χ^2/N (N is the number of degrees of freedom, χ^2/N should be close to 1, which in fact was always the case); the covariance matrix of the fitting parameters was calculated by the Monte Carlo method. Let us comment on the subtraction of the inelastic background and correction for instrument distortions.

We introduce the following terminology and notation. We call the spectral interval (E_1,E_2) occupied by true conversion lines the informative interval (Fig. 1). We denote by $I(E)$ the true conversion spectrum, by $Y(E)$ the sample spectrum (i.e., the spectrum $I(E)$ distorted by inelastic processes), and by $Q(E)$ the observed spectrum (i.e., the spectrum $Y(E)$ distorted by instrument factors). Here E denotes the kinetic energy of the electrons. By spectra we understand the corresponding probability distributions normalized in some convenient way. Accordingly, all equalities derived below must be understood as accurate to within arbitrary constant factors. We denote by $a(\xi)$ the instrument function of the spectrometer, responsible for the smearing of the spectrum by the instrument resolution. This function is assumed to be normalized to unity and not depend explicitly on the electron energy at entrance to the spectrometer. The tilde above the spectrum symbol denotes the corresponding spectrum smeared by the instrument resolution, i.e., $\tilde{Y}(E)=\int a(E-E')Y(E')dE'$, etc. Thus, assuming that $T(E)$ varies slowly in comparison with the width of the instrument function, it can be shown that

$$Q(E)=T(E)\tilde{Y}(E), \tag{1}$$

where $T(E)$ is the spectrometer transmission function, and

$$Y(E)=k(E)I(E)+\int_E^{E_2} I(E')R(E',E-E')dE'. \tag{2}$$

In Eq. (2) $k(E)$ is the probability of escape of a conversion electron with initial energy E from the sample without inelastic scattering, and $R(E',E-E')$ describes the shape of the inelastic tail for the conversion electrons with initial energy E'. We introduce the new functions

$$F(E)=k(E)I(E),\quad P(E',E-E')=[k(E')]^{-1}\times R(E',E-E'). \tag{3}$$

Assuming that the dependence of the function $P(E',E-E')$ on its first argument is weak in comparison with the width of the instrument function, it is not hard to show that

$$\tilde{Y}(E)=\tilde{F}(E)+\int_E^{E_2}\tilde{F}(E')P(E',E-E')dE'. \tag{4}$$

The function $\tilde{F}(E)$ has the following physical meaning: this is the spectrum of the electrons that have escaped from the sample without inelastic scattering (i.e., it is the elastic signal), smeared by the instrument resolution. Correspondingly, Eq. (4) also has a simple physical meaning, namely that the total signal leaving the sample ($\tilde{Y}$) is the elastic signal ($\tilde{F}$) plus the inelastic background (the integral), and the procedure for solving Eq. (4) for the spectrum $\tilde{F}$ if the spectrum $\tilde{Y}$ is known is to subtract out the inelastic background from the conversion spectrum.

Obviously, the spectrum $\tilde{F}(E)$, generally speaking, does not coincide with the true conversion spectrum $I(E)$. However, analyzing to first order we may limit the discussion to the spectrum $\tilde{F}(E)$ in place of $I(E)$ for the following reason. As Monte Carlo studies of the process of inelastic scattering of conversion electrons in a hydrocarbon film have shown[31] and as follows from experimental dependences of the electron mean free path on energy,[32] the function $k(E)$ is proportional with good accuracy to $I(E)$. The variability of $k(E)$ (on the order of 10% of the mean value over the informative spectral interval) is rooted in the systematic error of determining the line intensities.

Equations (1) and (4) make it possible from the observed experimental spectrum $Q(E)$ first to find the spectrum $\tilde{Y}(E)$ and then from the spectrum $\tilde{Y}(E)$ to find the elastic spectrum $F(E)$ if only the spectrometer transmission function $T(E)$ and the scattering function $P(E',E-E')$ are known. The procedure for determining the transmission function $T(E)$ is described in detail in Ref. 33. According to Ref. 33, the transmission function can be approximated by an exponential

$$T(E)\simeq\exp(\alpha E),\quad \alpha=-(1.69\pm0.05\pm0.17)\cdot10^{-2}\ \mathrm{eV}^{-1}. \tag{5}$$

To determine the scattering function it is necessary to study in detail the process of electron scattering in matter in terms of some microscopic model. However, reliable quantitative calculations of this kind are very complicated and probably cannot be carried out at the present time. Instead, it was shown in Ref. 34 that it is possible to introduce an effective phenomenological procedure for determining the scattering function. The following nontrivial circumstance suggests a suitable scattering function. It turns out that the low-energy side of the informative spectral interval (E_1, E_2) (Fig. 1) always adjoins a segment of inelastic background which grows nearly exponentially in the direction of lower electron kinetic energies. This allows us to choose the scattering function to be of the form

$$P(E-E')=\alpha_0 \exp[-\mu(E-E')]. \tag{6}$$

The constants a_0 and μ are easily determined from the amplitude of the spectrum at the point E_1 and the slope of the inelastic tail. Therefore, the problem of solving Eq. (4) becomes completely determined (the equation is easily solved by the method of simple iterations).

The question of systematic errors which can arise in the spectral line intensities in connection with the use of an approximate shape of the scattering function (6) was examined in two different ways in Refs. 34 and 31. In Ref. 34 an upper-bound estimate of the systematic errors was performed. The parameters of the scattering function were varied to the maximum extent possible, and it was observed how the conversion line intensities vary as a result. It was found that the mean variations of the intensities over all the lines used in the study and over all types of investigated extreme variations of the shape of the scattering function amounted to 0.7% of the total area of the conversion spectrum, and the maximum variations, to 2%. In Ref. 31 the procedure for subtracting out the background, based on the solution of Eq. (4) with scattering function (6), was applied to model spectra obtained from the initial spectra by modeling the passage of electrons through a hydrocarbon film using the Monte Carlo method. Since the exact form of the model elastic signal $F(E)$ in this case is exactly known, by comparing the result of background subtraction with the model elastic spectrum, one can estimate the systematic errors introduced into the line intensities by the implemented background subtraction algorithm. In this study the mean perturbation of the line intensities amounted to 0.3% of the area of the entire spectrum, and the maximum perturbation, to 0.7%. Generalizing the results of both methods, we may conclude that the algorithm of subtracting out the inelastic background can introduce an error in the spectral line intensities on the order of 1% of the total area of the spectrum, which amounts to roughly 5% of the intensities of the most important lines of the conversion spectrum of the uranium-235 isomer.

In Ref. 33 an analysis was performed of the total systematic error in the partial conversion probabilities obtained in the above-described procedure of mathematical spectral processing. Systematic errors associated with errors in the determination of the spectrometer transmission function (5), the approximate nature of the scattering function (6), and the approximation $k(E)=\text{const}$ were taken into account. It was found that the maximum relative error of the absolute values of the partial probabilities of conversion amounts to 12% for the most important spectral lines[2] ("$6p_{1/2}$," "$O2s$," and "$6p_{3/2}$," and the valence band VB). The error in the ratios of the partial probabilities of conversion can reach 25%, but this is relative to the case where we are comparing line intensities at opposite ends of the informative spectral interval, the distance between which amounts to roughly 25 eV. As the distance between the lines decreases, the error decreases proportionally. And finally, the error in the ratios of the intensities of lines belonging to different conversion spectra (i.e., corresponding to different chemical states of the uranium isomer) but corresponding to the same kinetic energy is less than 13%.

4. EXPERIMENT

There are a number of factors that make the preparation of samples with the uranium-235 isomer in a prescribed and controlled chemical state and in quantities sufficient for measurement of high-resolution conversion spectra a very difficult task. The main difficulties are connected with the very short mean free path of the soft conversion electrons, which hinders the use of samples prepared by chemical means. Another substantial complication is the fact that it is impossible to monitor the chemical state of the uranium isomer in the thin surface layer in any way independent of conversion spectroscopy, since we are talking here about fractions of a picogram of uranium in such a sample. In this connection, the main idea of the approach used below is to use those chemical states of the uranium isomer in which it naturally appears in the preparation of samples under the simplest and most reproducible conditions. It is only necessary to find those experimental conditions in which it is possible to obtain different conversion spectra and then in as detailed a way as possible to interpret the corresponding chemical states.

We have found that such states can be realized by using indium substrates to collect the ^{235m}U isomer. When collecting uranium isomer on an indium substrate by varying the discharge current in the accumulation chamber within the limits of 1 to 4 nA it is possible to alter the chemical state of uranium isomer within wide limits, as is indicated by the substantial change in the shape of the conversion spectrum. Some typical uranium isomer spectra, obtained in the collection of isomer on an indium surface for various discharge currents in the sample preparation chamber, are shown in Fig. 2 (here and in the remainder of this work the spectra are shown after correcting for instrument distortions and subtracting out the inelastic background). For spectrum a in Fig. 2 the discharge current was the smallest (1 nA), for spectrum d it was the largest (4 nA), and for the other samples it was intermediate. The form of the spectra in Fig. 2 suggests that the intermediate spectra (b and c) can be obtained simply as weighted sums of only two spectra $f_A(E)$ and $f_B(E)$, whose forms are similar, respectively, to spectra a and d in Fig. 2. We will refer to this conjecture as the hypothesis of two-component mixing. Our problem is to carry out a quantitative check of this hypothesis, to separate out the pure spectra f_A and f_B, and finally, to associate them with some chemical states A and B of the atoms of the uranium isomer. It is convenient to start with the last question.

Figure 3 shows two conversion spectra of uranium isomer near the ultimate possibilities realized in experiments with isomer collection onto an indium surface. It follows from the discussion of the structure of the samples in Sec. 2 that the chemical states A and B are uranium oxides. Indeed,

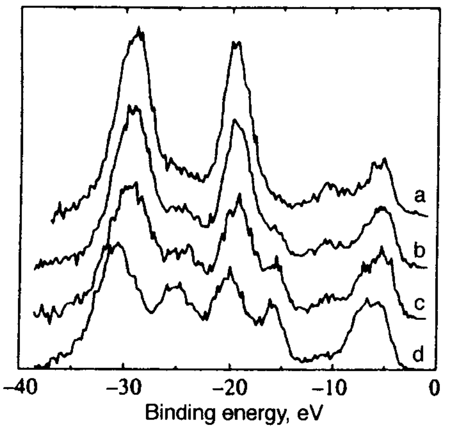

FIG. 2. Uranium-isomer conversion spectra recorded for collecting the isomer atoms on an indium surface at different discharge currents in an isomer collection chamber. Spectra a, b, c, and d correspond to currents of approximately 1, 2.5, 3.5, and 4 nA.

this is confirmed by the fact that the "O2*s*" line, which can be interpreted only as corresponding to the molecular orbital formed by hybridization of the 6*p* electrons of uranium and the 2*s* electrons of oxygen, is present in both spectra in Fig. 3 (Ref. 15).

In regard to the oxide corresponding to the spectrum f_B (similar to spectrum b in Fig. 3), we may draw some quite confident conclusions. The doublet structure in the region of the "$6p_{3/2}$" peak unambiguously indicates that we are dealing here with an atomic cluster based on the linear uranyl group O–U–O.[17,35] Moreover, from the separation between the components of the doublet (around 4.3 eV) it is possible to determine the distance between the oxygen and uranium atoms in uranyl to be 1.73±0.04 Å (Ref. 36). It is well known that in the formation of complexes in which uranyl participates, the uranyl group preserves a relative independence, and in the equatorial plane it may contain 4, 5, or 6 additional oxygen or halogen atoms.[37] These are all reasons for assuming that the f_B spectrum corresponds to the uranyl group coordinated by 4–6 oxygen atoms in the equatorial plane. Such an environment is similar to the environment of uranium in γ-UO$_3$, where the uranyl group is coordinated with four oxygen atoms. From the distance between the components of the "$6p_{3/2}$" doublet it is also possible to estimate the distance from the uranium atom to the equatorial oxygen atoms as 2.40±0.04 Å (Ref. 36).

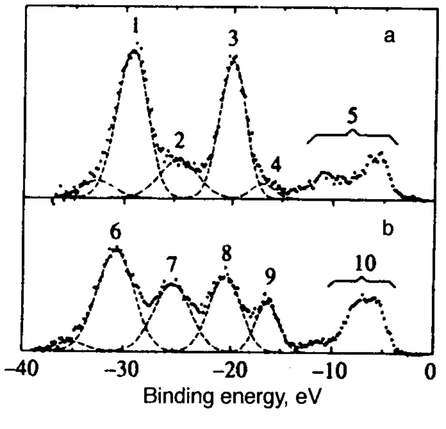

FIG. 3. Decomposition of uranium-isomer conversion spectra obtained for isomer atom collection on an indium surface. Annotation of the lines in the figure is as follows: *1, 6*—"$6p_{1/2}$," *2, 7*—"O2*s*," *3, 8*—"$6p_{3/2}(l)$," *4, 9*—"$6p_{3/2}(r)$," *5, 10*—*VB*. Spectrum *a* corresponds to the lowest experimentally observed degree of oxidation of the uranium isomer, and spectrum *b*, to the highest.

In regard to the oxide corresponding to the f_A spectrum (similar to spectrum a in Fig. 3), it is difficult to draw such definite conclusions. In spectrum a in Fig. 3 a weak trace of the right-hand component of the "$6p_{3/2}$" uranium line is visible, "$6p_{3/2}(r)$." However, the intermediate situation, when the right-hand component of the "$6p_{3/2}$" peak is present but has low intensity, does not correspond to any known simple oxide of uranium. A small admixture of the "$6p_{3/2}(r)$" component in experimental spectrum a in Fig. 3 is more simply explained by an admixture of the chemical state B to state A. Thus, in the chemical state A splitting of the "$6p_{3/2}$" uranium line is entirely absent; consequently, the uranium–oxygen cluster corresponding to state A has higher symmetry than the cluster corresponding to state B. Oxygen environments of uranium are known which can lead to such a result. This happens, for example, for the simple crystalline oxides UO$_2$ and UO with symmetry O_h (Ref. 38). Besides the higher symmetry of cluster A in comparison with cluster B, we may note a considerably weaker bond between uranium and oxygen in cluster A since the line of the conversion spectrum corresponding to the hybrid orbital U6*p*–O2*s* is significantly less pronounced. Just such behavior is to be expected for UO$_2$ and UO. All this indicates some kind of analogy between the chemical state A and uranium dioxide or monoxide.

By the relative intensity of the conversion line we mean the ratio of the area under the line to the area of the entire spectrum. Since the "$6p_{3/2}(r)$" line (Fig. 3) is present in the f_B spectrum and absent in the f_A spectrum (according to the proposed interpretation of the f_A spectrum), it is clear that the relative intensity of the "$6p_{3/2}(r)$" line in the mixed experimental spectrum characterizes the corresponding mixing coefficient of the A and B states. Moreover, if the relative intensity of the "$6p_{3/2}(r)$" line in the pure f_B spectrum is known (we denote it by P_B^0), then by an appropriate choice of the constructed procedure for extrapolating from the data set of experimental mixed spectra it should be possible to separate out the pure f_A and f_B spectra.

The magnitude of P_B^0 can be found from the uranium isomer conversion spectra measured during isomer collection onto a copper surface. Such spectra were examined in Ref. 33. The following two facts were established. First, during collection of isomer onto a copper surface the spectra always contain five characteristic peaks similar to the situation in Fig. 3b, i.e., similar to the spectrum f_B, where by varying the conditions of isomer collection it is not possible to change the shape of the spectra. Second, a specially constructed statistical analysis of the shape of the spectra showed that no other variations of the shape of the spectra from one measurement to the next are observed besides those associated with the Poisson electron counting statistics. These results may be interpreted as follows. Copper surfaces offer especially favorable conditions for formation of uranyl clusters; therefore the conversion spectrum observed for collection onto a copper surface is the spectrum of the pure B state. We will call this spectrum $f_{B(\mathrm{Cu})}$. We identify the relative intensity of the "$6p_{3/2}(r)$" line in the f_B spectrum with the corresponding quantity in the experimental $f_{B(\mathrm{Cu})}$ spectra. In Ref. 33 the result $P_B^0=(10.3\pm0.3)\%$ was obtained.

We next determine the relative intensity P of the "$6p_{3/2}(r)$" line for different mixed spectra from the indium surface and introduce the quantity

$$k=P/P_B^0. \tag{7}$$

Thus, in the examination of mixed spectra we proceed from the assumption that the value $k=0$ corresponds to the pure f_A spectrum and the value $k=1$ corresponds to the pure f_B spectrum.

We normalize the experimental conversion spectra to the corresponding total probabilities of conversion per unit time, which in the case of the uranium-235 isomer coincide with the decay constant of the isomer level. Let (E_i,E_f) be an arbitrary segment of the conversion spectrum. We consider a conversion spectrum f_k with the parameter k: $0\leqslant k\leqslant 1$. We denote by P_k, P_A, and P_B the integrals over the interval (E_i,E_f) respectively for the spectra f_k, f_A, and f_B. It is not hard to show that

$$P_k\simeq(1-k)P_A+kP_B, \tag{8}$$

where the deviation from exact equality in formula (8) may be neglected thanks to the small difference in decay constants of the uranium isomer in states A and B. We call the dependence of the area of a fixed segment of the spectrum on the parameter k the kinetic curve. The prediction of linearity of the kinetic curves (8), following from the hypothesis of two-component mixing, can be checked experimentally.

To use the formalism introduced above, the conversion spectra of the uranium isomer should be measured simultaneously with the decay constants. The technique of simultaneous measurement of the conversion spectrum and the decay constant was introduced by myself in Ref. 39. The essence of this technique is to measure the conversion spectrum in two stages, in two successive time intervals while the decay constant is determined by comparing the areas of the corresponding spectra calculated from the informative spectral interval (E_1,E_2) (Fig. 1). This guarantees that the decay constant and the conversion spectrum correspond exactly to the same chemical state of the uranium isomer.

Two series of measurements with collection of uranium isomer onto an indium surface constitute the experimental data base of the present work. In the first series, which we will call series T, thirty measurements of conversion spectra with simultaneous measurement of the decay constants were carried out. For technical reasons in this series of measurements there were time losses on the order of one half-life of the isomer; therefore, the series-T spectra are not very well statistically robust. In order to compensate for this deficiency of series T, a second series of measurements was carried out, which we will call series R, in which 29 spectra without simultaneous measurement of the decay constants with concomitant time losses were measured.

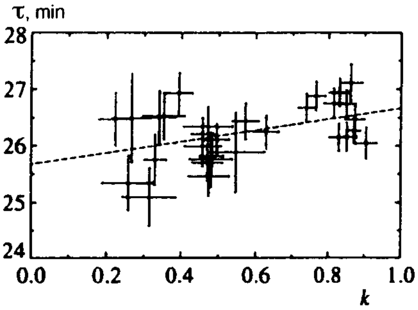

FIG. 4. Experimental points $\tau(k)$ for experimental series T and linear approximation by the maximum-likelihood method.

On the basis of the series-T experimental data we constructed an empirical dependence $\lambda(k)$, where λ is the decay constant and k is the parameter defined by formula (7). An empirical dependence was found in the form of a linear function from the experimental points $\lambda_{\mathrm{exp}}(k_{\mathrm{exp}})$ with the help of the maximum likelihood method. Figure 4 plots the corresponding experimental points and a straight-line fit (for convenience the corresponding half-lives τ rather than the decay constants λ are plotted along the ordinate). The dependence so obtained was then used to normalize the spectra of series R as well as series T.

We extended the obtained empirical dependence $\lambda(k)$ to $k=0$ and $k=1$, which gave the half-lives of the uranium isomer corresponding to the pure states A and B:

$$\tau_A=25.67\pm0.21 \text{ min}, \quad \tau_B=26.68\pm0.12 \text{ min},$$

$$(\tau_B-\tau_A)/\tau_A=(3.9\pm1.2)\%.$$

It makes sense to compare these values with the half-lives of the uranium isomer measured by de Mevergnies with massive samples of the chemically prepared compounds $^{235m}\mathrm{UO}_2$ and γ-$^{235m}\mathrm{UO}_3$ (Ref. 23):

$$\tau(\mathrm{UO}_2)=24.68\pm0.26 \text{ min}, \quad \tau(\mathrm{UO}_3)=26.06\pm0.08 \text{ min},$$

$$[\tau(\mathrm{UO}_3)-\tau(\mathrm{UO}_2)]/\tau(\mathrm{UO}_2)=(5.6\pm1.1)\%.$$

It is evident that the same trend of the half-life obtains both between UO_2 and γ-UO_3 and between the states A and B, and that the relative values of the half-lives in fact do not differ within the limits of experimental error. This confirms the reasonableness of interpreting state A as an analog of UO_2 and state B as an analog of γ-UO_3.

To check the hypothesis of two-component mixing, experimental kinetic curves were constructed for four segments of the conversion spectrum corresponding to the main conversion lines: "$6p_{1,2}$," "$O2s$," "$6p_{3/2}(l)$," and VB. Figure 5 plots the kinetic curves for the series-R measurements (for series T the curves have a similar form, but with larger statistical errors). Using the maximum likelihood method, we fit the kinetic data with straight lines. In the course of the fit we calculated the quantity

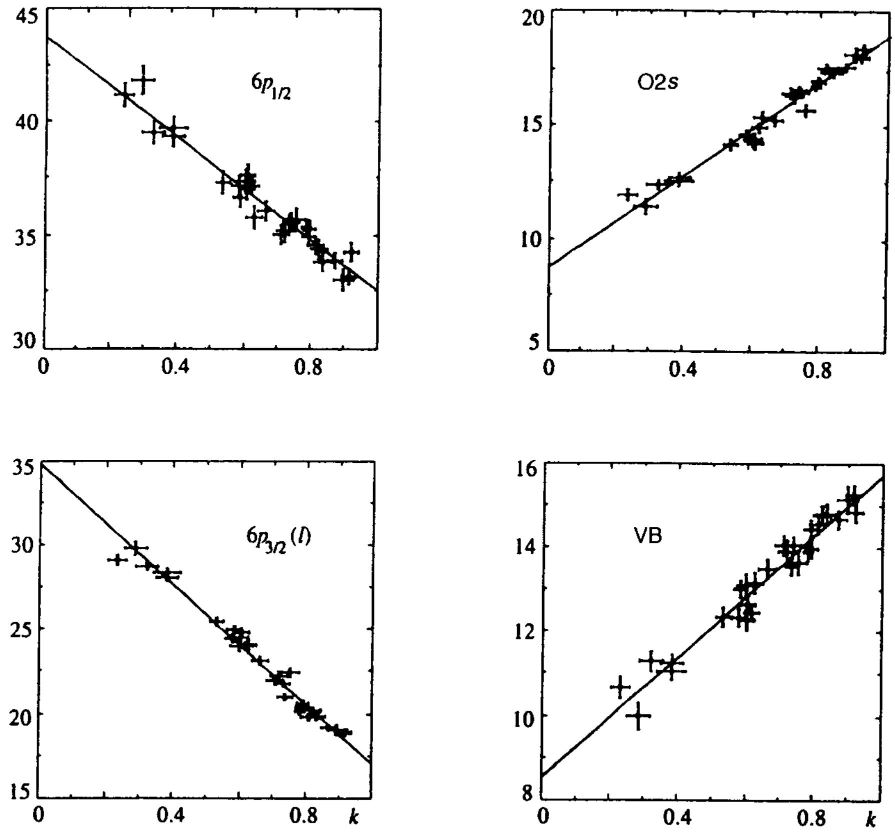

FIG. 5. Kinetic curves for experimental series R. The quantities plotted along the ordinates are the partial probabilities of conversion belonging to the indicated spectral regions (%).

$$\chi_c^2=\sum_i \frac{(a+bk_i-\lambda_i)^2}{\sigma\lambda_i^2+b^2\sigma k_i^2}, \tag{9}$$

which is an analog of the χ^2 parameter of the more familiar linear regression analysis. In formula (9) a and b are the fitting parameters of the linear dependence. Values of χ_c^2/N, where N is the number of degrees of freedom, are given in Table I for both series of measurements—T and R. The standard deviation for all values is equal to 0.26. From Table I it can be seen that there is not one significant deviation of χ_c^2/N from unity, i.e., there are no indications of deviations of the kinetic curves from a linear dependence. Thus, the hypothesis of two-component mixing is found to be well confirmed.

Formula (8) makes it possible to find the spectra f_A and f_B corresponding to the set of experimental mixed spectra in the maximum-likelihood sense. Toward this end, it is sufficient to construct the kinetic curves for each channel of the spectrum, to fit them with straight lines using the maximum likelihood method (8), and to extend each such straight line to $k=0$ and $k=1$. In order to track the reproducibility of the results, we processed the series-R and series-T spectra in this way separately. Figure 6 shows the pure spectra f_A and f_B, found from the mixed spectra of series R. The spectra found from series T have essentially the same form, but somewhat higher statistical spreading of the amplitudes. Fragments of the decompositions of the spectra into Gaussian lines corresponding to the region of inner valence molecular orbitals are shown in Fig. 6 by dashed lines.

TABLE I. Check of the hypothesis of two-component mixing of the spectra.

Series	Spectral region			
	U6$p_{1/2}$	O2s	U6$p_{3/2}(l)$	VB
T	0.89	0.78	1.23	1.23
R	0.87	1.05	1.24	1.19

Table II presents data on the structure of these spectra. The standard deviations of the line parameters, calculated by the Monte Carlo method, are indicated; systematic errors are not shown, but can be determined as in Sec. 3. For convenience, the partial probabilities of conversion are given in units in which $\lambda_B\equiv 100$. To convert to absolute probability values, it is necessary to multiply the corresponding data in

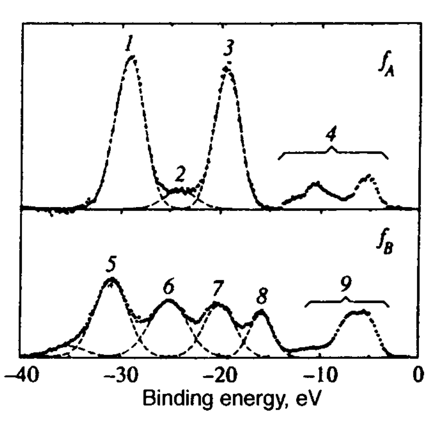

FIG. 6. Pure f_A and f_B spectra found from the series of experimental mixed spectra R. Annotation of the lines: 1—"$6p_{1/2}$," 2—"O2s," 3—"$6p_{3/2}$," 4—VB, 5—"$6p_{1/2}$" ($1S1u$), 6—"O2s" ($2S1u$), 7—"$6p_{3/2}(l)$" ($1S3u$), 8—"$6p_{3/2}(r)$" ($3S1u$), 9—VB.

TABLE II. Structure of pure f_A and f_B spectra. Each cell of the table contains (from top down): the partial probability of conversion in relative units, the line position (binding energy) in eV, and the line width in eV. The statistical errors are indicated in parentheses. Where the error is not indicated explicitly, it is approximately one significant digit. Rows $\langle A\rangle$ and $\langle B\rangle$ correspond to data averaged over series T and R.

	Line				
Spectrum	$6p_{1/2}$	O2s	$6p_{3/2}(l)$	$6p_{3/2}(r)$	VB
$A(T)$	44.6(0.4) 28.5 3.3	7.1(0.4) 23.7 4.4(0.4)	37.7(0.4) 18.6 3.1	0 - -	15.1(0.2) - -
$A(R)$	46.4(0.4) 29.3 3.5	6.2(0.5) 24.0 3.8(0.4)	37.2(0.4) 19.4 3.0	0 - -	15.2(0.2) - -
$B(T)$	31.5(0.2) 30.6 3.6	22.1(0.3) 24.8 4.3	16.4(0.3) 19.9 3.5	10.5(0.1) 15.3 2.7	19.2(0.2) - -
$B(R)$	30.7(0.3) 30.8 4.0	22.4(0.4) 25.0 4.5	16.9(0.3) 19.9 3.6	10.4(0.1) 15.8 2.7	19.0(0.1) - -
$\langle A\rangle$	45.5(0.3) 28.9(0.4) 3.4(0.1)	6.7(0.4) 23.9(0.2) 4.1(0.3)	37.5(0.3) 19.0(0.4) 3.1(0.1)	0 - -	15.2(0.1) - -
$\langle B\rangle$	31.3(0.2) 30.7(0.1) 3.8(0.2)	22.2(0.2) 24.9(0.1) 4.4(0.1)	16.7(0.2) 19.9(0.1) 3.5(0.1)	10.5(0.1) 15.6(0.3) 2.7(0.1)	19.0(0.1) - -
Cu(B)	31.4(0.5) 31.0 4.0	23.6(0.9) 25.1 5.0(0.4)	16.0(0.6) 19.9 3.4	10.3(0.3) 15.6 3.0	18.8(0.2) - -

Table II by 2.598×10^{-4} min. As a reference point for determining the binding energies, we used the position of the "$6p_{3/2}(l)$" line in the f_B spectrum, for which we adopted the value 19.89 eV. This energy is the averaged binding energy of the "U$6p_{3/2}(l)$" line found from x-ray electron spectroscopy data, determined from a set of 15 different uranyl compounds.[40] For convenience, the last line of Table II gives the breakdown of the $f_{B(\mathrm{Cu})}$ spectrum based on the data of Ref. 33. Notice that there is beautiful agreement between the parameters of the $f_{B(\mathrm{Cu})}$ and f_B spectra. This confirms that the B state on the indium surface and the state in which the uranium isomer always appears for collection onto a copper surface are indeed one and the same chemical state of the isomer as was assumed in the treatment of the series-T and R mixed spectra.

5. DISCUSSION: COMPARISON OF EXPERIMENT WITH CALCULATIONS OF THE ELECTRONIC STRUCTURE OF URANYL

It is well known that because the uranyl group possesses relative independence (stability) in the formation of the chemical bond, the main features of the x-ray electron spectra of uranyl compounds in the region of electron binding energies $\lesssim 40$ eV are determined specifically by the presence of this group.[17,35] This should hold to an even larger extent in the case of the conversion spectrum of uranium isomer. Therefore, to identify the lines of the f_B spectrum and to compare the results of experiment with the first-order theory we can apply the results of a calculation of the electronic structure of the isolated uranyl group. Here it is necessary to use relativistic calculations, since in the nonrelativistic calculations the $6p_{1/2}$ and $6p_{3/2}$ electrons do not differ while in the uranium atom they are separated in binding energy by the spin–orbit interaction by 10 eV and, what is most important, their single-electron conversion probabilities differ by more than a factor of two.[13]

A number of relativistic calculations of the electronic structure of uranyl are known.[41–45] All of them qualitatively reproduce the structure of the conversion spectrum f_B reasonably well in the region of the inner valence molecular orbitals (the lines "$6p_{1/2}$" through "$6p_{3/2}(r)$," Fig. 6) and agree with each other both in the order of sequence of the lines and in the makeup of the molecular orbitals in the sense of the method of linear combination of atomic orbitals (LCAO). Figure 6 identifies the lines of the f_B spectrum with the molecular orbitals of uranyl. The notation used corresponds to that in Refs. 44 and 45. Table III gives the structure of the inner valence molecular orbitals of uranyl in the terminology of the LCAO method according to Refs. 44 and 45.

It is clear directly from the shape of the f_A spectrum (Fig. 6) that the U6p electrons are much more weakly delocalized in the chemical state A of the uranium isomer than in state B. The intensity of the "O2s" line is so weak that it may be assumed that the "$6p_{1/2}$" orbital of compound A has essentially an atomic character and is therefore occupied by two U$6p_{1/2}$ electrons. Assuming a quasi-atomic nature of the "$6p_{1/2}$" orbital of compound A and using the results of the calculation of the electronic structure of uranyl given in Refs. 44 and 45, we can estimate how much the intensity of the "$6p_{1/2}$" conversion line in the f_B spectrum should vary in comparison with the f_A spectrum.

Reference 16 proposed an interpretation of the conversion spectra of soft nuclear transitions in terms of a "filling of the standard states in the conversion zone." In order to utilize the data calculated by the LCAO method[44,45] for a

TABLE III. Electronic structure of uranyl according to Refs. 44 and 45 and estimates of net occupancies of the molecular orbitals by the atomic electrons of uranium. The eigenenergy is normalized to the energy value −19.9 eV for the $1S3u$ orbital.

Spectral line f_B	Orbital	Energy, eV	Makeup of orbital (full Mulliken occupancies)	Overlap occupancy	Net occupancy
"$6p_{1/2}$"	$1S1u$	−33.3	$1.58(6p_{1/2})+$ $0.06(6p_{3/2})+$ $0.36(\mathrm{O}2s)$	0.292	$1.44(6p_{1/2})+$ $0.05(6p_{3/2})$
"O$2s$"	$2S1u$	−26.0	$0.33(6p_{1/2})+$ $1.09(6p_{3/2})+$ $0.48(\mathrm{O}2s)$	0.240	$0.30(6p_{1/2})+$ $1.00(6p_{3/2})$
none	$2S1g$	−23.7	$0.40(6d)+$ $1.58(\mathrm{O}2s)$	0.460	$0.17(6d)$
"$6p_{3/2}(l)$"	$1S3u$	−19.9	$1.91(6p_{3/2})+$ $0.09(\mathrm{O}2p)$	0.096	$1.86(6p_{3/2})$
"$6p_{3/2}(r)$"	$3S1u$	−13.5	$0.06(6p_{1/2})+$ $0.34(6p_{3/2})+$ $0.72(\mathrm{O}2p)+$ $0.83(\mathrm{O}2s)$	0.008	$0.06(6p_{1/2})+$ $0.34(6p_{3/2})$

comparison with the line intensities of the conversion spectrum, it is necessary to relate the formalism of Ref. 16 with concepts characteristic of the LCAO method.

Let some molecular orbital ϕ of uranyl in the LCAO representation have the form

$$\phi=\sum_l c_l^{\mathrm{U}}\chi_l^{\mathrm{U}}+\sum_m c_m^{\mathrm{O}}\chi_m^{\mathrm{O}}, \tag{10}$$

where χ_l^{U} are the atomic wave functions of uranium, χ_m^{O} are the atomic wave functions of oxygen, c_l^{U} and c_m^{O} are the coefficients of the linear combination. Since the probability of conversion on a neighboring atom is negligibly small,[16] to describe conversion it is sufficient to retain the terms in expression (10) belonging to the atomic orbitals of uranium. We thus obtain an expansion of exactly the same form as was investigated in Ref. 16. For this case it has been shown that the single-electron probability of conversion from the molecular orbital ϕ is given by

$$P_\phi^1=\sum_l |c_l^{\mathrm{U}}|^2 P_l^{\mathrm{U}}, \tag{11}$$

where P_l^{U} are the single-electron probabilities of conversion for the atomic orbitals of uranium. Using formula (11), we can write the total probability of conversion from the molecular orbital ϕ as

$$P_\phi=\sum_l N_l P_l^{\mathrm{U}}, \tag{12}$$

where the quantities N_l are the net occupancies of the molecular orbital ϕ by the χ_l^{U} electrons in the classification of occupancies given by Mulliken.[46]

Applying formula (12) and the assumption of the quasi-atomic nature of the "$6p_{1/2}$" line in the f_A spectrum, we find for the ratio of intensities of the "$6p_{1/2}$" lines in the f_B and f_A spectra

$$\frac{P_B(\text{``}6p_{1/2}\text{''})}{P_A(\text{``}6p_{1/2}\text{''})}=\frac{N_B(6p_{1/2})P(6p_{1/2})+N_B(6p_{3/2})P(6p_{3/2})}{2P(6p_{1/2})}, \tag{13}$$

where $P(6p_{1/2})$ and $P(6p_{3/2})$ are the single-electron probabilities of conversion on the $6p_{1/2}$ and $6p_{3/2}$ electrons in the isolated uranium atom, and $N_B(6p_{1/2})$ and $N_B(6p_{3/2})$ are the atomic net occupancies of the $1S1u$ molecular orbitals of uranyl.

We estimated the net occupancies from the data of Refs. 44 and 45 in terms of the total occupancies and overlap occupancies (Table III). Instead of the single-electron probabilities of conversion we used the single-electron conversion factors $w_e(6p_{1/2})$ and $w_e(6p_{3/2})$—dimensionless quantities proportional to the single-electron probabilities of conversion, which were calculated for the conversion transition of the uranium isomer in Ref. 13:

$$w_e(6p_{1/2})=4.81\cdot 10^5,\quad w_e(6p_{3/2})=2.16\cdot 10^5. \tag{14}$$

Calculations were performed in Ref. 13 with atomic wave functions in the Thomas–Fermi–Dirac and Hartree–Fock–Slater models. The values in Eqs. (14) are averages over these two models.

Using the data in Table III for the conversion factors (14) and the net occupancies used in formula (13), we find

$$\left.\frac{P_B(\text{``}6p_{1/2}\text{''})}{P_A(\text{``}6p_{1/2}\text{''})}\right|_{\text{theor}}=0.73, \tag{15}$$

whereas from the experimental data listed in Table II we obtain

$$\left.\frac{P_B(\text{``}6p_{1/2}\text{''})}{P_A(\text{``}6p_{1/2}\text{''})}\right|_{\text{exper}}=0.69\pm 0.01\pm 0.09. \tag{16}$$

The experimental (16) and theoretical (15) intensity ratios are found to be in beautiful agreement.

TABLE IV. Expected (''theoretical'') and experimental relative intensities of the conversion lines belonging to the inner valence molecular orbitals. The total errors (including systematic) are indicated in parentheses.

	''$6p_{1/2}$'' ($1S1u$)	''O2s'' ($2S1u$)	''$6p_{3/2}(l)$'' ($1S3u$)	''$6p_{3/2}(r)$'' ($3S1u$)
Calculation	44.9	23.0	25.7	6.5
Experiment	38.8(4.7)	27.5(3.3)	20.7(2.5)	13.0(1.6)

Analogously, it is possible to find the expected ratios of the line intensities of the f_B spectrum and compare them with the corresponding experimental values. The result of such a comparison is given in Table IV, where the sum of the line intensities belonging to the inner valence molecular orbitals is normalized to 100, both for the experimental and the theoretical values. In all cases, except for the ''$6p_{3/2}(r)$'' line, there is reasonable agreement between the experimental and calculated intensities. For the ''$6p_{3/2}(r)$'' line the calculated intensity is half the experimental value. However, the authors of Ref. 44 noted that taking the crystal field of the equatorial ligand-atoms of uranyl into account may increase the total occupancy of the $3S1u$ orbital by the $6p$ electrons from 0.4 (see Table III) to 0.8. Obviously, this would roughly double the estimate of the intensity of the ''$6p_{3/2}(r)$'' line in the f_B spectrum, as a result of which the agreement would improve. I will not attempt to compare theory and experiment in the valence-band region (VB, Fig. 6) since the accuracy of present-day calculations of the electronic structure in this region is not high.

Thus, reasonable agreement is observed between the expected and experimental intensities of the conversion lines in the conversion spectrum of uranium isomer in the region where calculations of the electronic structure appear to possess satisfactory accuracy. By virtue of the semi-quantitative character of the calculations, it is still difficult to speak of real agreement of theory with experiment; rather it may be stated that abrupt anomalies in the intensities of the conversion lines which might be linked with interference phenomena accompanying elastic scattering of conversion electrons are not revealed. We may conclude that the results obtained here do not contradict the assumption that the partial probabilities of conversion of uranium isomer remain proportional to the electron density at the nucleus as follows from the works of Grechukhin and Soldatov[13,16] and as is indirectly indicated by data on variations of the uranium isomer decay constant.[19–25] In the LCAO approximation this means that the partial probabilities of conversion are proportional to the atomic net occupancies of the molecular orbitals by the electrons that take part in conversion [formula (12)].

If we accept this conclusion, then the question arises why the strong interference effects in the conversion probabilities predicted in Ref. 26 are not manifested in experiment. It is obviously necessary to search for mechanisms that can lead to the suppression of interference of conversion electrons. I considered this question in Ref. 29. In this work, I showed that it is possible to point to at least two mechanisms which were not taken into account in Ref. 26 and which can in general lead to suppression of interference effects in conversion spectra: thermal vibrations of atoms and inelastic scattering of conversion electrons. Qualitative estimates in Ref. 29 showed that one can expect a roughly fivefold suppression of the contribution of interference effects to the partial probabilities of conversion of uranium-235 isomer, which implies a radical suppression of the effects predicted in Ref. 26. Consequently, the probabilities of conversion can remain proportional to the electron density at the nucleus with an accuracy of 5–10%, and the original version of the theory of Grechukhin and Soldatov holds with the same accuracy.[13,16]

In this light, a decrease in the intensity of the ''$6p_{1/2}$'' line in the f_B spectrum in comparison with the f_A spectrum by roughly 30% may be considered as an indication of migration of U$6p_{1/2}$ electrons with binding energy around 30 eV to the hybrid molecular orbitals. With the help of formula (12) we can obtain an estimate of the number of electrons that have migrated over to the hybrid molecular orbitals (in the terminology of the LCAO method). We obtain 0.6 electron for the electrons that have migrated over and 1.4 electrons for those remaining in the initial ''quasi-atomic'' orbital.

Note that except for conversion spectroscopy of uranium-235 isomer, at present there exists no experimental method that allows one to obtain such detailed information about the partial occupancies of the inner molecular orbitals of heavy-element compounds. Potential competitors of conversion electron spectroscopy in this region are x-ray or ultraviolet electron spectroscopy and x-ray emission spectroscopy. However, photoelectron spectroscopy does not possess selectivity to the contributions of different types of electrons to the molecular orbitals; therefore, generally speaking, the line intensities of the photoelectron spectrum do not give direct information about the structure of the corresponding molecular orbital. X-ray emission spectra, in principle, contain the same information, but in the case of heavy elements, in particular uranium, they have such a complicated structure[47] that it is still difficult to pose the question of quantitative analysis of such spectra.

It should be noted that conversion spectroscopy of uranium isomer still faces a number of complicated unresolved problems. The most urgent among them are the construction of a quantitative theory of conversion which would permit an accurate estimate of the contribution to conversion both of interference effects and effects suppressing interference, and on the experimental plane, the development of a technique for preparing samples with uranium isomer in a prescribed atomic environment. On the other hand, it has been possible to solve a number of fundamental questions in the way of transforming conversion spectroscopy of uranium isomer into a fully capable, quantitative method for investigating the electronic structure of matter, and on this path the first substantial results have been obtained.

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1) By line widths we everywhere understand here the full-widths at half maximum.

2) We put spectral line symbols of the type "$6p_{1/2}$" in quotation marks because the spectral lines correspond not to pure atomic electrons, but to hybrid molecular orbitals.

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