Influence of chemical environment on the conversion-electron spectrum of the *E*3 transition in ^{99m}Tc

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In order to investigate the influence of the chemical environment on the conversion of the *E* 3 transition in ^{99m}Tc we have measured the conversion and x-ray photoelectron spectra of $(NH_4)_2TcBr_6$, Tc_2S_7, and $KTcO_4$. We have calculated theoretically the electronic structure and conversion probabilities for the anions TcO_4^- and $TcBr_6^{2-}$ in the framework of a relativistic variant of the X_α scattered-wave technique. The data obtained give an idea of the nature and magnitude of the changes in the conversion process for various chemical surroundings of the technetium atom, they contain valuable information on the electronic structure of the chemical compounds, and in particular they indicate directly the substantial participation in the chemical binding of the Br4*s*, S3*s*, and O2*s* electrons.

1. INTRODUCTION

The isomeric state ^{99m}Tc presents extensive possibilities for study of the influence of the physical and chemical states of the technetium atom on the decay process. Several workers[1,2] have studied the influence exerted on the decay constant λ by the chemical environment, pressure, temperature, and electric fields. The experimentally observed values of $\Delta\lambda/\lambda$ vary over the range $1\cdot10^{-5}$–$4\cdot10^{-3}$, and the largest values are obtained as the result of change of the chemical environment.[3–7]

Values of $\Delta\lambda/\lambda$ give only an integrated picture of the variations of the conversion process, since $\Delta\lambda/\lambda$ is the sum of partial values $\Delta\lambda_i/\lambda$ for individual electron orbitals. The structure of the orbitals and their contributions to the conversion may differ substantially in different chemical environments.[8,9] Considerably more detailed information on the structure of the atomic electron shells in matter is contained in the conversion-electron spectrum, which is resolved into individual lines corresponding to conversion from individual electron orbits.[10,11]

We have previously studied[12,13] the conversion-electron spectra of the *E* 3 transition in ^{99m}Tc in metallic form[1)] [^{99m}Tc] and in $NH_4[^{99m}Tc]O_4$. The results of those studies indicate good qualitative agreement between the theoretical picture of the conversion process[8,9] and the experimental information. In the present work we have investigated the conversion-electron spectra of ^{99m}Tc in $(NH_4)_2[^{99m}Tc]Br_6$, $[^{99m}Tc]Tc_2S_7$, and $K[^{99m}Tc]O_4$, and also the corresponding x-ray photoelectron spectra. We have also made theoretical calculations of the electronic structure and the conversion probabilities for the anions TcO_4^- and $TcBr_6^{2-}$ in the framework of a relativistic variant of the method of X_α scattered waves.

2. EXPERIMENTAL PART

2.1. Measurement of spectra

The conversion and x-ray electron spectra were measured in a HP5950A. Hewlett-Packard electrostatic x-ray photoelectron double focusing spectrometer. The energy resolution of the apparatus was constant over the entire range of energies and equal to about 1 eV. The electron energy scale of the apparatus was calibrated on the basis of standard x-ray photoelectron lines[15] with accuracy of 0.2 eV or better. The residual gas pressure in the working chamber of the spectrometer was about $2\cdot10^{-9}$ Torr. The measurement technique has been described in more detail in a previous article.[12]

2.2. Preparation of conversion-electron sources

The mean free path of electrons with energy about 2 keV in matter up to the first inelastic collision is extremely small and is equal to several tens of angstroms. This determines the features of methods of preparation of conversion-electron sources. They should provide concentration of the isomer ^{99m}Tc in a small volume, purification from contaminants contained in the initial product, the required chemical form, and uniform distribution of the material on the substrate within the source dimensions.

$[^{99m}Tc]Tc_2S_7$. To 10 cm^3 of the product obtained from the technetium source and containing ^{99m}Tc in the form of sodium pertechnetate in 0.45% water solution of NaCl we added several tens of micrograms of $NH_4{}^{99}TcO_4$ (as carrier) and 1.5 cm^3 of concentrated HC1. Technetium heptasulfide was then deposited from the solution, heated to a temperature about 90 °C, by passing through it hydrogen sulfide for a period of an hour with subsequent jointing.[16] The deposit was washed in 0.1N HCl and then in doubly distilled water, deposited from water suspension on an aluminum substrate, and then dried.

$(NH_4)_2[^{99m}Tc]Br_6$. For about 20 hours before the series of measurements, the column of the technetium concentrator with a sorbent containing ^{99}Mo was washed with distilled water. The isomer ^{99m}Tc was washed out with portions of distilled water of 1 cm^3 each. The portions (usually the second, third, and fourth) containing the main part of the isomer were combined, a $K^{99}TcO_4$ carrier was added ($\approx$0.2 mg of Tc), the solution was evaporated for an hour at a tempera-

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ture of about 90 °C (to carry out isotopic exchange) to ≈ 1 cm^3, and then transferred to a cell for electrolysis. Distilled water (to a total volume of 4 cm^3) and H_2SO_4 were added to the cell to pH = 1. Electrolysis was carried out for about 1.5 hours at a current of about 200 mA onto a platinum substrate with a Teflon mask of diameter 4 mm. The metallic $[^{99m}Tc]$ deposited on the substrate was carefully washed with distilled water and dried. Then the $[^{99m}Tc]$ was dissolved on the substrate in several drops of hydrogen peroxide (i.e., it was converted[16] to $H[^{99m}Tc]O_4$), one drop of solution of $(NH_4)_2{}^{99}TcBr_6$ ($\approx 0.2\,\mu g$ of Tc) in concentrated HBr was added, and the content of the substrate was evaporated in HBr vapor to 1–2 drops. Here[16] the $H[^{99m}Tc]O_4$ was converted to $H_2[^{99m}Tc]Br_6$ and then as the result of isotopic exchange to $(NH_4)_2[^{99m}Tc]Br_6$. A second platinum substrate was moistened with ethylene glycol (to provide uniform distribution of the source material over the moistened surface of the substrate), and on it was deposited the content of the first substrate, which was then evaporated to dryness in HBr vapor at a temperature ≈ 75 °C. During the evaporation crystallization of $(NH_4)_2[^{99m}Tc]Br_6$ took place, and the acid $H_2[^{99m}Tc]Br_6$ evaporated.

$K[^{99m}Tc]O_4$. Potassium pertechnetate was prepared in the same way as $(NH_4)_2[^{99m}Tc]Br_6$. However, in the solution instead of $(NH_4)_2{}^{99}TcBr_6$ we added one drop of solution of $K^{99}TcO_4$ ($\approx 0.2\,\mu g$ of Tc) in water, and the evaporation was carried out without HBr vapor. Here as the result of isotopic exchange the $H[^{99m}Tc]O_4$ was converted to $K[^{99m}Tc]O_4$. During evaporation to dryness crystallization of $K[^{99m}Tc]O_4$ took place, and the acid $H[^{99m}Tc]O_4$ evaporated.[16]

The chemical state of the sources was monitored by x-ray photoelectron spectroscopy, which permits identification of the chemical state of technetium.[17] Comparison of the x-ray electron spectra of the sources and those of standard compounds confirms the correspondence of the quantitative content and chemical state of technetium and the other chemical elements present in the sources to the corresponding characteristics of the standard compounds (see Figs. 1 and 2). The correspondence of the chemical states of ^{99}Tc and ^{99m}Tc for each type of source was confirmed by observation of identical chemical shifts of the binding energy of the inner electrons of technetium in the conversion and x-ray electron spectra in the transition from one chemical state of the sources to another (see Figs. 2 and 3 and Ref. 17). The differences observed in Figs. 1 and 2 of the x-ray electron spectra of the sources and the standard samples are explained in the following way.

The presence of the O1*s* and C1*s* peaks in Fig. 1 is explained by contamination of the sample surfaces.[12] The rise of the intensities of these peaks in the spectra of the sources is due to the decrease of the amount of material in the sources with a maintained level of surface contamination. This leads also to appearance in the spectra of peaks of the substrate material. Adsorption of HBr on the surface of the source is responsible for the greater intensity of the bromine peaks in $(NH_4)_2[^{99m}Tc]Br_6$ in comparison with $(NH_4)_2TcBr_6$ (Fig. 2). In the sources of $K[^{99m}Tc]O_4$ we observed impurities of Na,

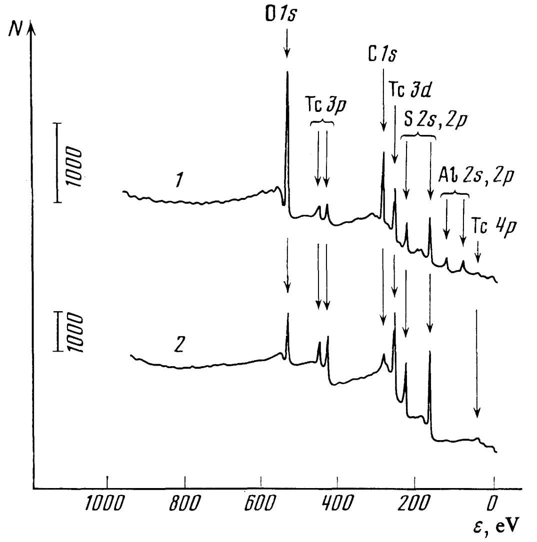

FIG. 1. Compiled x-ray photoelectron spectra from a $[^{99m}Tc]Tc_2S_7$ source on Al (1) and from a standard sample of Tc_2S_7 (2). In this and the other figures ε is the electron binding energy, *E* is the conversion electron kinetic energy, and *N* is the number of counts.

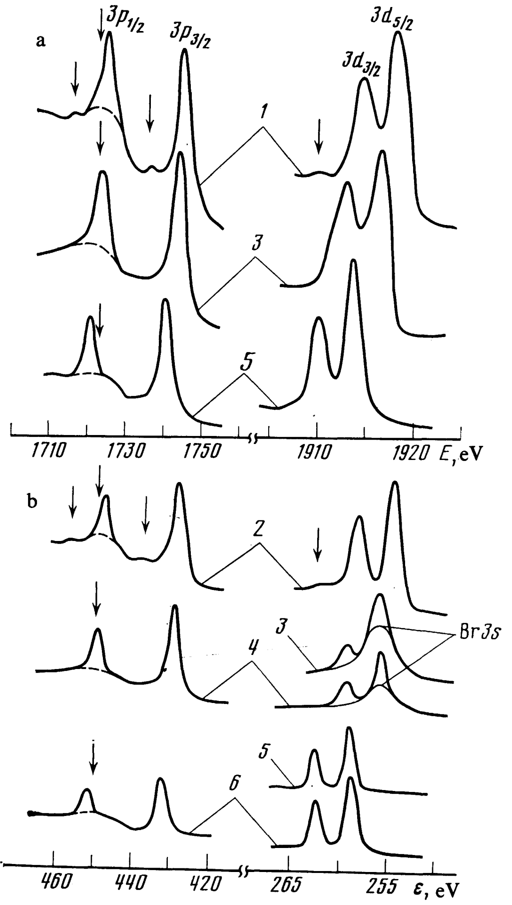

FIG. 2. a—Conversion spectra, b—x-ray photoelectron spectra, in the region of the 3*p* and 3*d* electron peaks of technetium from the following sources: 1—$[^{99m}Tc]Tc_2S_7$, 3—$(NH_4)_2[^{99m}Tc]Br_6$, 5—$K[^{99m}Tc]O_4$, and from the following standard samples: 2—Tc_2S_7, 4—$(NH_4)_2TcBr_6$, 6—$KTcO_4$.

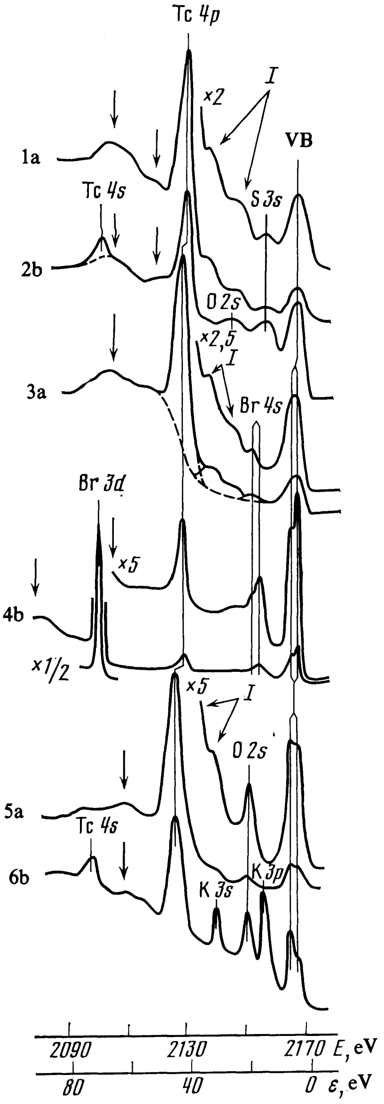

FIG. 3. Structure of the following spectra: a—conversion spectra b—x-ray photoelectron spectra, in the region of the outer electron peaks from the following sources: 1—$[^{99m}Tc]Tc_2S_7$, 3—$(NH_4)_2[^{99m}Tc]Br_6$, 5—$K[^{99m}Tc]O_4$ and from the following standard samples: 2—Tc_2S_7, 4—$(NH_4)_2TcBr_6$, 6—$KTcO_4$. The notation in the figure is as follows: VB—valence band, I—Auger peaks $L_3M_{4,5}M_{4,5}$ associated with conversion transitions in ^{99m}Tc with energy near 140 and 142 keV.

Ca, and Mg which did not affect the chemical state of the technetium.

3. THEORETICAL PART

At the present time there is only one series of calculations of conversion probabilities in technetium compounds.[8,9] These calculations were carried out according to the following scheme.

First the electronic structure of the investigated anion was calculated in the framework of the nonrelativistic X_α scattered-wave technique, and the partial densities of the *s*, *p*, *d*, and *f* types in a technetium sphere were calculated for each molecular orbital. Then the probability of conversion in a given orbital was calculated as the sum of the probabilities of conversion in *p* and *d* atomic orbits of technetium with appropriate weights. The probabilities of conversion in the atomic orbitals were calculated with relativistic atomic wave functions. To use these probabilities in the present calculation scheme it was therefore necessary to average them over the total angular momentum of the electron.

This scheme of calculation, it appears to us, is not internally consistent and systematic. This is due first of all to the relativistic nature of the conversion process. In fact, the conversion occurs mainly near the nucleus in a sphere with radius of the order of the radius of the *K* orbit (~ 0.01 Å for technetium).[11,18] In this region the Coulomb field of the nucleus with a scale of $0.1\ mc^2$ or more is acting on the electron. Therefore relativistic effects play a substantial role in the conversion process.

Proceeding from this fact, we developed a relativistic variant of the X_α scattered-wave technique, based on the Dirac equation (a detailed description can be found in a preprint[19]). On the basis of this technique we calculated the electronic structures of the anions TcO_4^- and $TcBr_6^{2-}$. The geometrical parameters of the anions were taken identical to those adopted in Ref. 8. The conversion probability was calculated in the approximation of nonpenetration (as in Ref. 10). Here the wave functions of the emitted electron were calculated in the field only of the technetium atom. This approximation is justified since according to the theory of EXAFS[20] the order of magnitude of effects associated with allowance for neighboring atoms for an electron in the continuum is determined by the factor $1/(pR)^2$, where p is the wave number of the electron and R is the distance between atoms; in our case this factor is $\lesssim 10^{-5}$. The integration in calculation of the conversion matrix elements was carried out over the volume of the technetium sphere. Since internal conversion is highly localized, there is no need of extending the integration to a larger region.

4. RESULTS AND DISCUSSION

1. In Figs. 2–4 we have shown all conversion peaks and the corresponding portions of the x-ray electron spectra of the compounds studied. The spectra have much in common. In particular, for the inner electrons in the transition from one compound to another the same chemical shifts (in energy) are observed. The structures of the spectra of the inelastically scattered electrons which accompany the photoelectron and conversion-electron peaks are practically identical. The most intense peaks of the inelastically scattered electrons are shown in Figs. 2 and 3 by the vertical arrows. In those cases in which they coincide with the primary-electron peaks, the maxima of the loss spectra are identified by dashed lines (Figs. 2–4).

However, in the x-ray photoelectron spectra, in contrast to the conversion spectra, a number of additional lines are observed (see Fig. 1) in accordance with the chemical composition of the sources, the impurity layers, and the substrates. (A review of the conversion spectrum of metallic technetium has been given previously.[12] Compilations of the spectra of the compounds studied in the present work for the inner lines differ from the spectrum of Ref. 12 only in the structure and intensity of the inelastic loss spectrum and in the presence of a chemical shift. The spectra of the outer

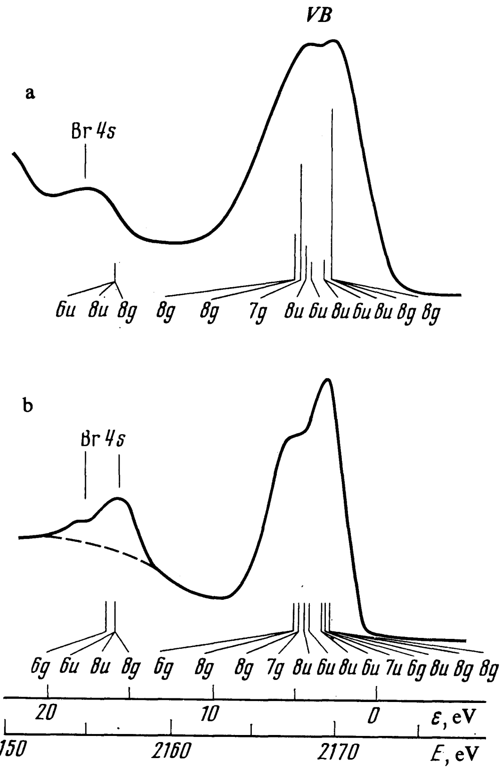

FIG. 4. Comparison of experimental spectra in the region of the outer electron peaks: a—conversion spectrum for a $(NH_4)_2[^{99m}Tc]Br_6$ source, b—x-ray photoelectron spectrum for a standard sample of $(NH_4)_2TcBr_6$ with theoretical values for the anion $TcBr_6^{2-}$. Classification of the molecular orbitals was carried out on the basis of the irreducible representations of the double group O_h' (see Ref. 21).

electrons are given in Fig. 3.) This difference is explained by the difference in the physics of the phenomena of nuclear conversion and the photoelectric effect. In contrast to conversion, the photoionization process is practically unlocalized. In addition, the conversion process for the E3 transition occurs practically only on the electrons with orbital angular momenta $l = 1$ and 2 (for the case of technetium), since conversion on electrons with $l = 0$, 3, and 4 is negligible. Therefore the conversion spectra contain the peaks of those electron orbitals which have an appreciable p and d electron density near the technetium nucleus.

2. In the table we have given the results of quantitative analysis of the experimental conversion spectra, together with the results of theoretical calculations. The relative line intensities obtained directly from the experimental spectra are given in the lines of the table marked with the number 0. In the lines marked with the number 1 we have given the experimental relative conversion probabilities obtained after use of Eq. (14) from Ref. 22 to take into account the influence of inelastic scattering in the source material on the relative intensities of the conversion-spectrum lines. Here the probable errors due to the influence of the matrix effect are negligible under the conditions of our experiment. In practice the error values calculated with this formula do not differ from those used previously.[12,13]

In agreement with the theoretical predictions, the experimental values of the relative conversion probabilities for the inner $3p$ and $3d$ lines (see the table) are constant within the experimental error (according to the data of the present work and the data obtained previously[12,13]). The calculation

TABLE I.

		Intensities relative to $3p_{3/2}$ line ($\times 100$)				
		$3p_{1/2}$	$3d$	$4p$	Э^{*}_{ns}	Valence band
$(NH_4)_2[^{99m}Tc]Br_6$ (experimental, present work)	0	56.7±1,0	53,7±0.9	30,1±1.1	0.92±0.10	5,8±0.3
	1	57,2±1.0	48,6±1.0	24,7±1.2	0.87±0.09	4,6±0,3
$_{99m}TcBr_6^{2-}$ (theoretical, present work)		56,4	47.4	24.7	0,06	3,0
$TcBr_6^{2-}$ (theoretical, Ref. 8)		56,3	53,7	25.0	0,16	3.8
$[^{99m}Tc]Tc_2S_7$ (experimental, present work)	0	56,5±0.8	53,4±0,7	29.4±0,9	$0{,}5\ \pm^{0{,}2}_{0{,}1}$	5.0±0,3
	1	57.0±0.8	48.3±0.9	24,1±1,2	$0{,}4\ \pm^{0{,}2}_{0{,}1}$	4,0±0,3
$K[^{99m}Tc]O_4$ (experimental, present work)	0	56.2±1.5	52.9±1.3	28,9±1.0	2.3±0,4	4.4±0.3
	1	56.7±1,5	47,8±1.4	23,7±1.2	1.8±0.3	3,5±0.3
$NH_4[^{99m}Tc]O_4$ (experimental, Ref. 13)	0	55.5±2	52.4±3	29.4±1.7	2,7±1.0	4.8±0.5
	1	56.0±2	47.4±2.8	23.8±1,7	2.2±0.8	3,8±0.5
$_{99m}TcO_4^-$ (theoretical, present work)		56.7	47,4	25,5	0,76	2.71
TcO_4^- (theoretical, Ref. 8)		56.3	53,7	25.2	0,92	3,38
$[^{99m}Tc]_{metal}$ (experimental, Ref. 12)	0	56,6±1,8	52,1±0,9	32,3±2.2	–	5,5±0,4
	1	57,0±1.8	47,2±1,0	26.1±2,3	–	4,4±0,5
$^{99m}Tc_{metal}$ (theoretical, Ref. 9)		56,3	53.6	24.4	–	4.36
$^{99m}Tc_{atom}$ (theoretical) present work**		56,6	47,4	25,7	–	2.1
$^{99m}Tc_{atom}$ (theoretical) [5]		56,3	53,7	25.8	–	2,9
$^{99m}Tc_{atom}$ (theoretical) [10]		56.5	48.3	26,0	–	2,3
$^{99m}Tc_{atom}$ (theoretical) [23]		56,6	48.1	26,1	–	2.3
$^{99m}Tc_{atom}$ (theoretical) [24]		56,6	47,0	–	–	–

* Э_{ns} =Br4s, S3s, O2s.

**Calculations similar to those made in Ref. 10 except that in obtaining the atomic potential the value $\alpha = 0.7035$ was used for the coefficient in the exchange term instead of $\alpha = 1$ as used in Ref. 10.

of Nagel *et al.*[5] for the free technetium atom, and correspondingly the calculations of Refs. 8 and 9 which use the results of Nagel's calculation as initial data in evaluating the influence of the chemical environment, give an exaggerated relative probability of conversion for 3*d* electrons. Our results for anions, and also calculations of other authors[10,23,24] for atoms, which use a description of the states of the electron emitted in conversion different from that used in Ref. 5, are in better agreement with experiment (see Table I and also Ref. 12).

3. The spectra of the outer electrons are given in Fig. 3. The most interesting feature of the conversion spectra is the observation in them of peaks arbitrarily designated S 3*s*, Br 4*s*, and O 2*s* (since their position corresponds to the position of the peaks of the x-ray electron spectra produced mainly by S 3*s*, Br 4*s* electrons).

According to our calculations and those of Ref. 8 the appearance of these peaks in the conversion spectra is due to a substantial rearrangement of the electron structure (formation of molecular orbitals) of the outer shells of the technetium atom and its immediate environment. The O2*s* peak of the conversion spectrum corresponds to conversion in a molecular orbital formed, according to the calculation of Ref. 25, more than 90% as the result of O2*s* electrons and about 5% as the result of Tc4*d* electrons. We shall consider the results for each of the compounds investigated.

The conversion spectrum of $K[^{99m}Tc]O_4$ follows in its main details the $NH_4[^{99m}Tc]O_4$ spectrum obtained by us previously.[13] The relative intensities of the conversion peaks are also in good agreement. This result, and also the measured values of $\Delta\lambda/\lambda$ from Refs. 3 and 4 for pertechnetates relative to technetium sulfide, apparently indicate a relatively weak influence of the cation on the conversion process, although the differences in the x-ray electron spectra of $KTcO_4$ (see Fig. 3) and NH_4TcO_4 (Ref. 13) are quite substantial.

The appearance in the conversion spectrum of $[^{99m}Tc]Tc_2S_7$ of the S3*s* peak indicates a significant hybridization of the 3*s* electrons of sulfur with the outer electrons of technetium. In determining the intensity of this peak it is necessary, however, to take into account the probable contribution to the peak area of a satellite which accompanies all peaks of the inner lines of the sulfide spectra and is removed from them by about 10 eV (see Figs. 2 and 3). The probable origin of the satellite is in inelastic discrete energy loss or processes of the shakeup type (see for example Ref. 26). The magnitude of the contribution was determined from the ratio of the areas of the Tc4*p* peak and its satellite and the area of the valence-band peak. The intensities obtained are given in the table. The presence in the sulfide conversion spectrum of the S3*s* peak with the intensity given in the table shows that the influence of the chemical environment of the technetium atom in this case is not at all small, as might be supposed on the basis of data on the change of the decay constant in the sulfide with respect to metallic technetium (see Refs. 3 and 4).

An interesting result was obtained for ammonium hexabromotechnetate. In Fig. 4 we have compared the experimental spectra with theoretical values for the anion $TcBr_6^{2-}$. The results of the calculations are shown in the form of line spectra located above the experimental x-ray electron and conversion spectra, and the ratio of the heights of the calculated conversion spectrum corresponds to the ratio of the theoretical partial conversion probabilities. Matching on the binding energy scale was accomplished from the position of the valence-band peaks. The x-ray electron spectrum shows for the Br4*s* peak the presence of some structure, which agrees qualitatively with the theoretical results. However, the experimental splitting of the components of the peak is considerably greater than the theoretical value. In addition, in the conversion spectrum we observe only one component, which corresponds to the component of the x-ray electron spectrum with the largest binding energy. A difference in the shape of the valence-band peaks is also evident. This difference in the spectra is apparently explained in the following way. Actually the region of the peaks of the x-ray electron spectrum, the valence band, and the peak arbitrarily designated by us as Br4*s* contains information on the entire set of molecular orbitals, the formation of which involves not only the electrons of technetium and bromine but also those of hydrogen and nitrogen. The conversion spectrum selects from this set only those orbitals which have definite properties (see subsection 1 of section 4). In particular, according to the theory the conversion for the anion $TcBr_6^{2-}$ occurs with appreciable probability only in 13 of the 17 molecular orbitals formed by the outer electrons of technetium and bromine (see Fig. 4). Here the probability of conversion will depend strongly on the degree of localization of the electron density of the orbital near the technetium nucleus.

Thus, the difference in the spectra is explained by the fact that the x-ray electron spectrum gives the whole picture of the electron orbitals of $(NH_4)_2TcBr_6$, while the conversion spectrum separates from it the part which characterizes the chemical binding only between the technetium atoms and their surroundings.

The results of our calculation are insufficient for interpretation of the x-ray electron spectrum, but like the calculations of Ref. 8 they agree qualitatively with the structure of the conversion spectrum. Quantitatively, however, a considerable discrepancy is observed in the region of the Be4*s* peak (by more than a factor of ten), and also for the valence-band peak (about one and one-half times). It should be mentioned that the theoretical intensities of the conversion lines of the outer electron states, both in $TcBr_6^{2-}$ and in TcO_4^-, turn out to be underestimated in comparison with experiment (see Table I).

This situation can be explained if one assumes that the potential acting on the electron in a real anion differs substantially from a potential of muffin-tin type, i.e., there are small potential valleys between the atoms of the anion, along which electrons travel relatively easily from atom to atom.

4. It is of interest to clear up the question of the possibility of experimental study of the degree of hybridization of the deeper electron shells of technetium.

Since in the case of 4*p* electrons the conversion probability can change appreciably only as the result of their delocalization, the most likely procedure here is to search for changes of the structure of the peak in the conversion spectra of specially chosen compounds. In the case of 4*s* electrons the situation is different. In the free technetium atom, as we have already pointed out, conversion on *s* electrons essentially does not occur. However, if a substantial degree of hybridization is possible for 4*s* electrons in some chemical environment, then the molecular orbitals formed in certain cases apparently can have an appreciable fraction of *p* and *d* electron density (relative to technetium). In this case such molecular orbitals can be observed in the conversion spectrum. Elucidation of this question may be helped by a sufficiently accurate theoretical calculation. For solution of this problem experimentally it is necessary to be able to take into account accurately the background from the inelastic loss spectrum and other possible phenomena.

In the present work the possibility of existence of significant hybridization could be suggested for the Tc4*s* and Br3*d* electrons (difference in binding energy 2.7 ± 0.2 eV) in $(NH_4)_2[^{99m}Tc]Br_6$. However, in the conversion spectra we do not see corresponding sufficiently intense peaks which could be distinguished in the background of the inelastic loss spectrum (see Fig. 3).

We should mention also the interesting special case which occurs in this same compound. From data on the x-ray electron spectra for compounds containing $TcBr_6^{2-}$ it follows that the binding energies of the $Tc3d_{5/2}$ and Br3*s* electrons are about 256.2 eV (Ref. 17) and differ by an amount 0.1 ± 0.2 eV, i.e., a situation close to resonance is observed. Therefore we undertook a special study of the conversion spectrum of the 3*d* line for this compound. However, no deviations of the shape of the 3*d* peaks from the ordinary shape were observed for the spin-orbit doublet with a ratio of the intensities of the $3d_{3/2}$ and $3d_{5/2}$ components equal to 0.67.[10,5]

5. The data obtained permit us to form an idea of the nature and magnitude of the actual changes of the conversion spectrum of the E3 transition in ^{99m}Tc in various chemical environments. These changes are explained practically completely by rearrangement of the electronic structure and by differences in the degree of localization of the outer electrons of technetium and the neighboring atoms. The magnitude of the changes is considerably greater than that predicted by the calculations. The relatively small values of the measured $\Delta\lambda/\lambda$ are explained by mutual compensation of the partial values $\Delta\lambda_i/\lambda$.

A similar pattern of conversion is observed in the case of conversion in transitions of other isotopes, for which extensive information on variations of λ has been obtained in recent years.[1,2] It is clear that for a correct interpretation of these data it is necessary to have information on the electronic structure of the conversion-electron sources. This is true also in regard to interpretation of changes in conversion spectra studied with resolution poorer than a few tens of eV.

The combined study of conversion and x-ray electron spectra provides valuable information of the electronic structure of chemical compounds, and on the local behavior of the electron density near the technetium nucleus. The experimental results and the theoretical calculations directly indicate a substantial involvement of the O2*s*, S3*s*, and Br4*s* electrons in the chemical binding.

Comparison of theoretical calculations and experimental data has shown the high sensitivity of the conversion method of study of the electronic structure of matter to the details of the behavior of the electron density.

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[1)] The designations of the chemical compounds of various isotopic compositions are given in accordance with the rules adopted by the IUPAC.[14]

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