Effect of chemical environment on the conversion-electron spectrum of the $E3$ transition of ^{99m}Tc in ammonium pertechnetate and in metallic technetium

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The conversion and x-ray electron spectra of ammonium pertechnetate were measured with an aim at investigating the influence of the chemical environment on the conversion of the $E3$ transition of ^{99m}Tc. These spectra are compared with the metallic-technetium spectra previously obtained by us. A peak not observed in the conversion spectrum of metallic technetium is seen in the conversion spectrum of ammonium pertechnetate. This demonstrates directly the participation of the $2s$ electrons of the oxygen in the chemical bond with the outer technetium electrons. The results of a quantitative analysis in conjunction with data of theoretical calculations performed for atomic technetium, the TcO_4^- anion, and metallic technetium in the cluster approximation, permit a quantitative estimate of the rearrangement of the structure of the electronic orbitals in NH_4TcO_4 and metallic Tc compared with atomic Tc.

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1. INTRODUCTION

The isomer ^{99m}Tc is one of the nuclei for which an influence of the physical and chemical conditions on the decay process has been experimentally observed.[1] The influence of the chemical environment on the decay constant of ^{99m}Tc was investigated in Refs. 2–5. At the same time, in cases similar to ^{99m}Tc, measurement of the conversion electrons should be an effective method of investigating the influence of the chemical environment.[6] This is attested to by the results of recent measurements of the conversion spectrum of ^{235m}U in γ-UO_3 and UF_4 (Ref. 7) and the results of the theoretical calculations of the partial probabilities of the conversion of the $E3$ transition of ^{99m}Tc in TcO_4^-, TcF_6^{2-}, $TcCl_6^{2-}$, $TcBr_6^{2-}$, TcI_6^{2-} (Ref. 8) and in metallic technetium.[9]

We have investigated in this study the influence of the chemical environment on the spectrum of the conversion electrons of the $E3$ transition of ^{99m}Tc in ammonium pertechnetate NH_4TcO_4 and in metallic Tc. We measured for this purpose the conversion and x-ray electron spectra of the ammonium pertechnetate. The obtained spectra are compared with one another and with the corresponding spectra of metallic technetium, which were investigated by us earlier,[10] as well as with the results of theoretical calculations.

2. EXPERIMENT

The conversion and x-ray electron spectra were measured with the Hewlett-Packard HP5950 double-focusing electrostatic x-ray electron spectrometer. To measure the conversion spectra, the energy range of the spectrometer was extended to higher electron kinetic energies by suitably changing the electric potentials on the electrodes of the electron-optical system. The energy resolution of the instrument is constant at ~1 eV in the entire energy range. The electron-energy scale of the instrument was calibrated against standard x-ray electron lines[11] with accuracy not worse than 0.2 eV. The residual-gas pressure in the working chamber of the spectrometer was $\sim 2 \times 10^{-9}$ Torr.

Sources in the form of $NH_4Tc(^{99m}Tc)O_4$ were prepared of metallic Tc (^{99m}Tc) by treating it with HNO_3 vapor and then by NH_3. The metallic Tc (^{99m}Tc) was deposited on a platinum substrate just as in Ref. 10, by an electrolysis method.[12] The chemical state of the sources was monitored against their x-ray electron spectrum by comparison with the x-ray electron spectra of polycrystalline NH_4TcO_4 of high degree of purity.

The experimental procedure is described in greater detail in Ref. 10.

3. RESULTS AND DISCUSSION

Figures 1–3 show the conversion and x-ray electron spectra of both ammonium pertechnetate and of metallic technetium. It is seen that there is good qualitative agreement between both types of spectra. On going from metallic technetium to the ammonium pertechnetate, the peaks of the both of the x-ray electron and of the conversion spectra are shifted by ~5 eV towards higher binding energies (see Figs. 1 and 2 and Table I), i.e., a chemical shift is observed. The structure of the spectra of the inelastically scattered electrons, which accompany the peaks of the photoelectrons and of the conversion electrons, is practically the same. The

TABLE I.

		Photoelectron binding energy, eV			Kinetic energy of the ions and electrons, eV		
		$\varepsilon_{NH_4TcO_4}$	$\varepsilon_{Tc\ metal}$	$\Delta\varepsilon$	$E_{NH_4TcO_4}$	$E_{Tc\ metal}$	ΔE
Tc	$3s_{1/2}$	550.9±0.5	545.6±0.3	5.3	–	–	–
	$3p_{1/2}$	452.1±0.2	447.4±0.2	4.7	1720.5±0.3	1725.1±0.2	4.6
	$3p^*_{3/2}$	432.4±0.2	427.6±0.2	4.8	1740.3±0.3	1744.9±0.2	4.6
	$3d_{3/2}$	262.5±0.2	257.5±0.2	5.0	1910.1±0.2	1915.3±0.2	5.2
	$3d_{5/2}$	258.9±0.2	253.9±0.2	5.0	1913.8±0.2	1918.9±0.2	5.1
	$4s_{1/2}$	74.6±0.2	69.5±0.2	5.1	–	–	–
	$4p$	45.1±0.2	40.1±0.3	5.0	2127.3±0.3	2131.8±0.3	4.5
Maxima of valence band		7.6±0.3	2.0±0.3	–	2165.5±0.4	2169.8±0.3	–
		5.0±0.3	–	–	–	–	–
O	$1s_{1/2}$	530.6±0.2	–	–	–	–	–
	$2s_{1/2}$	21.9±0.3	–	–	2151.1±0.4	–	–
N	$1s_{1/2}$	401.2±0.2	–	–	–	–	–

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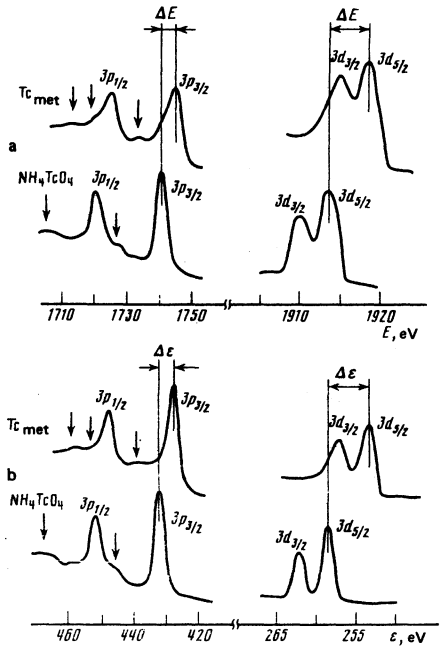

FIG. 1. Conversion (a) and x-ray electron (b) spectra of NH_4TcO_4 and of metallic technetium in the region of the peaks of the $3d$ and $3p$ electrons of technetium.

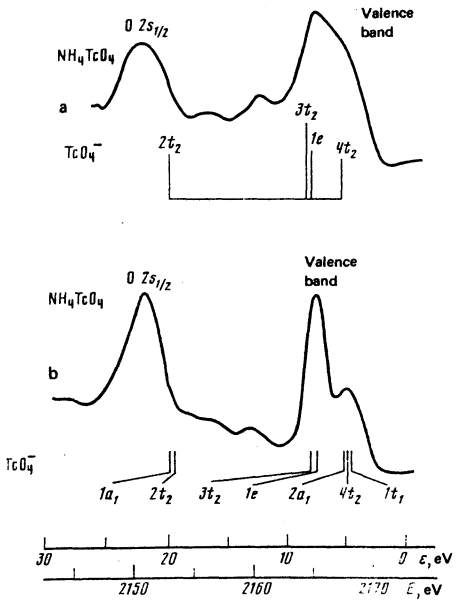

FIG. 3. Comparison of the experimental conversion (a) and x-ray electron (b) spectra of NH_4TcO_4 in the region of the outer-electron peaks with the theoretical-calculation data[8] for the TcO_4^- in liquid.

most intense maxima of the spectrum of the inelastically scattered electrons are marked in Figs. 1 and 2 by arrows.

Just as for metallic technetium,[10] a comparison of the conversion spectrum with the x-ray electron spectrum for NH_4TcO_4 makes it easy to separate the $3p_{1/2}$-, $3p_{3/2}$-, $3d_{3/2}$-, $3d_{5/2}$-, $4p_{1/2,3/2}$ and valence-electron conversion

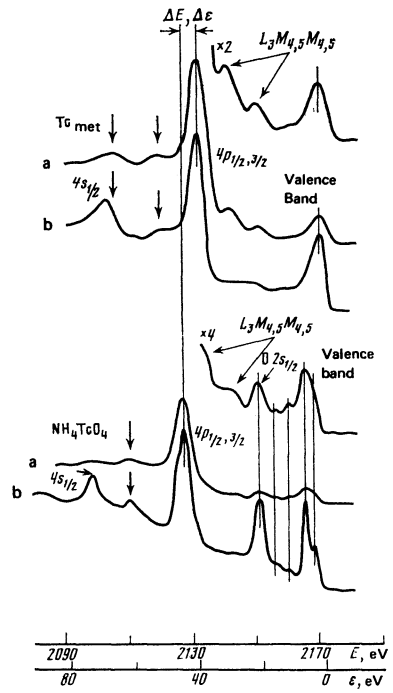

FIG. 2. Structure of the conversion (a) and x-ray electron (b) spectrum in the region of the outer-electron peaks of NH_4TcO_4 and metallic Tc.

peaks. In accordance with the calculation data[13,8] owing to the low conversion probability, no peaks of $3s$ and $4s$ electrons were observed in the spectrum. The Auger peaks due to the conversion of the ^{99m}Tc transitions with approximate energy 140 and 142 keV in ammonium pertechnetate relative to metallic technetium experience a chemical shift approximately equal to the chemical shift of the conversion lines.[14]

The most interesting feature of the conversion spectrum of NH_4TcO_4 is the observed peak arbitrarily marked O $2s_{1/2}$ in Figs. 2 and 3. It corresponds in position to the x-ray electron spectrum peak connected mainly with the O $2s$ electrons. This peak has no analog in the conversion spectrum of metallic technetium. Its appearance, in our opinion, is due to the influence of the chemical environment on the process of conversion of the $E3$ transition of ^{99m}Tc in NH_4TcO_4. Since the process of conversion of the $E3$ transition of ^{99m}Tc, in contrast to the photoeffect used in x-ray electron spectroscopy, is localized in practice in a sphere of radius 0.2 Å around the technetium nucleus[13] (see also Ref. 15), the appearance of this peak in the conversion spectrum is direct evidence that $2s$ electrons of oxygen are present near the technetium nucleus.

The effect observed was explained in fact in Ref. 8, in which were calculated the electron structure and the partial probabilities of the conversion of the $E3$ transition of ^{99m}Tc for TcO_4^- in the liquid phase by the X_α scattered-wave method. The formation of molecular orbitals TcO_4^- is connected with a substantial rearrangement of the electron structure of the outer shells of the free atoms of technetium ($4d, 5s, 5p$) and oxygen ($2s, 2p$). The probability of conversion on the molecular orbitals is determined by the presence in them of p- and d-electron density localized near the technetium nucleus. Therefore (see Ref. 8) the conversion in TcO_4^- takes

place in "its own valence band" on the molecular orbitals $3t_2$ and $4t_2$ (produced by Tc $5p$ and O $2p$ electrons) and $1e$ (produced by Tc $4d$ and O $2p$ electrons), and also on the relatively deeper $2t_2$ molecular orbital (more than 90% of which is due to O $2s$ and approximately 5% to the Tc $4d$ electrons[16]). The probability of conversion on $1t_1$, $2a_1$, and $1a_1$ molecular orbitals is negligibly small.

A comparison of the calculated data of Ref. 8 with the experimental spectra for NH_4TcO_4 is given in Fig. 3. The calculation results are shown in the form of line spectra located under the experimental x-ray electron and conversion spectra, the ratio of the heights of the lines of the calculated conversion spectrum corresponding to the ratio of the theoretical partial probabilities of the conversion. In the comparison, the position of the orbitals $3t_2$ and $1e$ on the energy scale is made to coincide with the position of the maximum of the valence band in the spectra. It is seen that in its basic details the structure of the experimental spectra agrees qualitatively with the calculation data. The observed differences, in particular, can be attributed to the difference between the electronic structures of NH_4TcO_4 and TcO_4^-.

The transition from the free technetium atom to the metal is also connected with a substantial rearrangement of the electron structure (see the calculation of Ref. 9). The chemical environment has a particularly strong influence on the outer electrons. The p states which are not occupied in the technetium atom become filled in the valence band of the metal, the density of the valence d electrons near the nucleus increases. As a result, the probability of conversion on valence electrons increases by ~50% compared with the free technetium atom.[9] For the $4p$ electrons, the calculations[9] indicates, in contrast to the calculation of Ref. 13, a noticeable delocalization and a decrease of the conversion probability. According to the calculation data in Refs. 8 and 9, the probability of conversion on the inner $3p$ and $3d$ electrons is practically independent of the chemical environment.

Table II shows the results of a quantitative analysis of the experimental conversion spectra, and the theoretical calculation data for comparison. The influence exerted on the ammonium-pertechnetate conversion-spectrum relative line intensities by the effects of elastic scattering of the electrons in the source material and in the contamination layer was taken into account in the same manner as for metallic technetium.[10]

We estimate now the agreement between the experimental and theoretical conversion pictures. In accord with the prediction of the calculations, the experimental bodies of the $3d$-doublet intensities relative to the $3p_{3/2}$ line for NH_4TcO_4 and metallic technetium are constant within the limits of the errors indicated in Table II. However, calculation[4] for the free technetium atoms and accordingly the calculations of Refs. 8 and 9, which use the results of the calculation of Ref. 4 as the initial data for the estimate of the influence of the chemical environment, overestimate the relative conversion probability for the $3d$ electrons. We note that in a number of studies[6,17,18] where a different approximation was used to describe the states of the electron, the theoretical values obtained for the free atom (see Table II) agree with experiment (see also Ref 10). For NH_4TcO_4 the relative conversion probability for the O $2s$ line exceeds the theoretical value obtained for the $2t_2$ orbital TcO_4^- by a factor 1.5–3 (with account taken of the measurement error). For the remaining lines, the experimental conversion probabilities given in Table II agree within the limits of the measurement errors with the theoretical ones both for the metallic technetium and for the ammonium pertechnetate.

TABLE II. Intensity relative to the $3p_{3/2}$ line (× 100).

		Intensity relative to the $3p_{3/2}$ line (× 100)					
		$3p_{1/2}$	$3p_{3/2}$	$3d$	$4p$	O $2s$	valence band
NH_4TcO_4 (experiment, present paper)	0	55.5±2	100	52.4±3	29.4±1.7	2.7±1	4.8±0.5
	1	56.0±2	100	47.4±2.8	23.8±1.7	2.2±0.8	3.8±0.5
TcO_4^- (theor.[8])		56.3	100	53.7	25.2	0.92	3.38
Tc metal (exper.[10])	0	56.6±1.8	100	52.1±0.9	32.3±2.2		5.5±0.4
	1	57.0±1.8	100	47.2±1.0	26.1±2.3		4.4±0.5
Tc metal (theor.[9])		56.3	100	53.6	24.4		4.36
Tc_{atom} (theor.[4])		56.3	100	53.7	25.8		2.9
Ref. 6		56.5	100	48.3	26.0		2.3
Ref. 17		56.6	100	48.1	26.1		2.3
Ref. 18		56.6	100	47.0			

Note. Here 0 labels the relative line intensities and 1 the experimental values of the relative conversion probabilities.

According to the theoretical data, the relative probability of conversion on the valence electrons increases substantially on going from the free atom to the metal and to TcO_4^- (from 2.9 to 4.36 and 3.38). The corresponding experimental relative conversion probabilities are 4.4 ± 0.5 and 3.8 ± 0.5 and are in good agreement with the theoretical predictions concerning the character of the variation of these quantities. The insufficient measurement accuracy does not permit definite conclusions to be drawn concerning the character of the changes of the relative probabilities of the conversion on $4p$ electrons. At the same time, for $4p$ and valence electrons, owing to the low difference between the kinetic energies of the conversion lines, the relative conversion probabilities are practically equal to the relative line intensities. We shall use this circumstance. For NH_4TcO_4, our experimental data yield $(I_{val}/I_{4O})_{exp} = 0.162 \pm 0.015$. The corresponding theoretical value is 0.134. For the metal we obtain respectively 0.170 ± 0.012 and 0.179. The theoretical value for the free atom is 0.112 (Ref. 4). We see that for a metal the agreement between experiment and calculation is good. The experimental results for ammonium pertechnetate seem to indicate a stronger influence of the chemical environment on the conversion spectrum than given in Ref. 8.

The results of the foregoing comparison indicate a good qualitative correspondence between the theoretical picture of the conversion process and the experimental. The method of the X_α scattered waves on the whole takes correct account of the features of the electronic structure of those chemical compounds which are responsible for the influence of the chemical environment on the conversion process.

It must be emphasized that a study of the conversion-electron spectra yields different information on the electronic structure of the compounds than that contained in the x-ray electron spectra. The difference is due to the fact that the conversion process is strongly localized near the excited nucleus, whereas the photoeffect does not have this property. In other words, the conversion method can provide information on the local behavior of the electron density near the nucleus. In this respect, the situation is similar to that obtaining in the study of the Knight shift, but the latter characterizes the change of the total density of all the s electrons, whereas an investigation of the conversion spectra yields the change of the electron density of a given level, which need not necessarily be the s level (one level type is separated for practically each nuclear transition type, s, p, or d).

We note in conclusion that the internal-conversion method can be useful for a probing of the spatial structure of molecular orbitals (this is demonstrated by the fact that an O $2s$ line was observed in the conversion spectrum of NH_4TcO_4), a fact of undoubted importance for the investigation of the nature of the chemical bond and for a verification of various theoretical calculation methods in quantum chemistry and in solid state physics.

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