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Estimation of Chemical Effect on the Decay Rate of ^{99m}Tc

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The chemical effect on the decay rate of the 2.17-keV isomeric transition of ^{99m}Tc has been studied theoretically. Simplified estimation of the effect is presented, where calculations of the internal-conversion probabilities for various subshells are made and the relative change in λ for two kinds of pairs are estimated. The results are $\lambda(\mathrm{TcO_4^-})-\lambda(\mathrm{Tc_2S_7})=3.27\times10^{-3}\lambda(\mathrm{Tc_2S_7})$ and $\lambda(\mathrm{Tc_2S_7})-\lambda(\mathrm{metal})=3.15\times10^{-4}\lambda(\mathrm{metal})$. The present theoretical treatments are not accurate enough for the quantitative discussion, but give the reasonable explanation to the experimental results.

KEY WORDS: Radioactivity ^{99m}Tc / Calculated $T_{1/2}$ / Chemical effect /

I. INTRODUCTION

Since the discovery of radioactivity, it has been believed that decay rates of radioactive materials are constant and can not be affected by any external condition. Therefore, the suggestion by Segrê[1] and Daudel[2] in 1947 that in the case of nuclear decays involving the orbital electrons, the decay rate might be altered by an external influence, drew a strong attention to physicists. There are two types of decays where the orbital electrons directly concern the nuclear decay, *i. e.*, the electron capture decay and the internal conversion.

The most interesting case is $^{99m}\mathrm{Tc}(T_{1/2}=6.0\mathrm{h})$. This isomer is the second excited state decaying to the ground state $^{99}\mathrm{Tc}(T_{1/2}=2.12\times10^5\mathrm{y})$ through a cascade nuclear transition, of which the transition energies are 2.17 and 140.5 keV, respectively. The isomeric transition of ^{99m}Tc to the first excited state has an E3 character and proceeds almost completely by the internal conversion, where the conversion can take place only in the M and N shell due to its low transition energy. This indicates that the change in the conversion probability (or decay rate) may be observable when the isomer is in different environmental conditions. The earliest experiment with ^{99m}Tc was by Bainbridge *et al.*[3,4] Using three kinds of Tc samples (metallic Tc, $\mathrm{Tc_2S_7}$, $\mathrm{KTcO_4}$), they compared the difference in their decay rates and have established the experimental evidence that the nuclear decay rate can be altered chemically. Recently, we have measured[5] the relative change in the decay rate λ of ^{99m}Tc having three different chemical forms

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(metallic Tc, Tc_2S_7, ϕ_4AsTcO_4). Our results essentially agree well with those by Bainbridge *et al.*[3,4]

However, because of the difficulty in theoretical treatments, up to the present only one simple theoretical estimation has been reported by Slater.[6] Introducing the concept of the atomic bond length and using the fact that the Tc-O bond length in $KTcO_4$ is smaller than the Tc-Tc distance in Tc metal, he claimed that the Tc atom is squeezed more in $KTcO_4$ and that this squeezing effect gives rise to a larger conversion probability of the 2. 17-keV transition in $KTcO_4$.

In the present work, a more realistic model is used. First, the states of valence electrons in the chemical compounds are estimated by the use of the molecular orbital theory. Second, the atomic potential corresponding to the estimated valence electron states is calculated. Then the states of core electrons are estimated by using this atomic potential, and calculations of the internal-conversion probability for various shells are made. The theoretical model presented here gives the reasonable explanation to our experimental results reported in the previous paper.[5]

II. THEORETICAL

The accurate estimation of the chemical effect on λ is very difficult. However, if we are interested only in the relative magnitude of λ between different chemical environments, it is possible to make approximate estimations of this effect. In this paper, we present rough theoretical estimations of the chemical effect on λ in three different states; metallic Tc, Tc_2S_7, and TcO_4^-. For the latter two compounds, the electronic structures were calculated by the molecular orbital (MO) theory. There have been developed several MO theories for analysis of the molecular structures of chemical compounds. Of these models, we used the simplest approach, the extended Hückel method (EHMO).[7] In most MO theories, the molecular orbitals are expressed as the linear combinations of atomic orbitals (AO) of the valence electrons in the atoms which constitute the molecule:

$$\Psi_i=\sum_{\mu} c_{\mu i}\phi_{\mu}, \tag{1}$$

where Ψ_i is the MO and ϕ_μ is the AO. We use the Roman suffix to denote the MO, while the Greek suffix represents the AO. The coefficient $c_{\mu i}$ is to be determined as that the total electronic energy of the valence electrons in the molecule becomes minimum.

In the EHMO theory, the Hamiltonian of the system is approximated by the one-electron Hamiltonian, H_{eff}, and the interaction between electrons is taken into account implicitly. This assumption simplifies the problem and the equation to be solved is of the from

$$(H-ES)C_i=0, \tag{2}$$

where C_i represents the column vector $c_{\mu i}$, E is the energy eigenvalue, and the overlap integrals are given by

$$S_{\mu\nu}=\int\phi_{\mu}\phi_{\nu}d\tau. \tag{3}$$

The matrix elements of the Hamiltonian are expressed as

$$H_{\mu\nu}=\int\phi_\mu H_{eff}\phi_\nu d\tau. \qquad (4)$$

In Eq. (4), the Coulomb integrals are chosen as

$$H_{\mu\mu}=-I_\mu, \qquad (5)$$

where I_μ is the valence orbital ionization potential for the atomic orbital μ. On the other hand, the resonance integrals ($\mu\neq\nu$) are approximated as

$$H_{\mu\nu}=0.5K(H_{\mu\mu}+H_{\nu\nu})S_{\mu\nu}. \qquad (6)$$

The constant K is taken to be 1.75.

Then the orbital energies are given by roots of the secular equations [Eq. (2)] and the coefficients $c_{\mu i}$ are obtained for the corresponding eigenvalues. Using $c_{\mu i}$ and $S_{\mu\nu}$, the AO populations are calculated in the following form:

$$P_\mu=2\sum_i^{occ}\sum_\nu c_{\mu i}c_{\nu i}S_{\mu\nu}, \qquad (7)$$

where the summation $\sum_i^{occ}$ runs over occupied molecular orbitals only. The value P_μ obtained by Eq. (7) can be considered as the number of valence electrons in the atomic orbital μ.

The above calculations have been made by the use of the Slater-type orbital (STO) for the AO's.[8] The overlap integrals were evaluated from the table of Lofthus.[9] In the original STO's, instead of principal quantum number n, non-integer n^* is used in the power of r. However, we used n (=4) instead of n^* (=3.7) for $4d$ shell of Tc as well as $5s$ and $5p$ shells, because $S_{\mu\nu}$ can not be evaluated analytically for non-integer n^*.

The electronic structure of the TcO_4^- ion is known to be a regular tetrahedron with Tc-O distance of 1.75 Å.[10] On the other hand, to the authors' knowledge, no report has so far been published for the crystal structure of Tc_2S_7. In rough approximations, however, we may replace Tc by Re and S by O, respectively. This assumption is supported by the fact that the ions TcO_4^-, ReO_4^-, and ReS_4^- have the similar molecular structure.[11]

Krebs *et al.*[12] determined the crystal structure of Re_2O_7 by X-ray diffraction. According to their results, the structure consists of strongly distorted ReO_6 octahedra connected to fairly regular ReO_4 tetrahedra. We used their data of Re_2O_7 for calculations of the electronic structure of Tc_2S_7. The calculated values of P_μ for the valence electrons in TcO_4^- and Tc_2S_7 are listed in Table I. The P_μ values for TcO_4^- indicate that the Tc atom is in the form of Tc^{+7}. This value are in agreement with the usually adopted value of the charge on Tc in TcO_4^-, +7. On the other hand, the charge on Tc in Tc_2S_7 is slightly less than zero. This may be due to many assumptions made by us because of lack of the data for the crystal structure. However, the present result sug-

Table I. The AO Populations P_μ for Tc Atom in TcO_4^- and Tc_2S_7

Shell	TcO_4^-	Tc_2S_7
$4d$	0.0162	6.742
$5s$	0.0415	0.309
$5p$	0.1640	0.035

gests that the charge on Tc is much smaller in Tc_2S_7 than in TcO_4^-.

The AO populations in the Tc atoms obtained from the MO calculations have been used to modify the atomic potential estimated from the self-consistent-field (SCF) calculations. For this purpose, the nonrelativistic SCF calculations were performed for free Tc atoms by the use of the modified version of the computer program developed by Herman and Skillman.13) A natural Tc atom has a ground-state electronic configuration of $(4d)^5(5s)^2$, but in the chemical compounds one of $5s$ electrons is considered to be promoted into $5p$ state. Therefore, we made the SCF calculations for the configuration of $(4d)^5(5s)(5p)$.

In this SCF program, the Hartree-Fock-Slater (HFS) approximation is used and the presence of other electrons is taken into account through the exchange potential:

$$V_{EX}(r) = -6\left[\frac{3}{8\pi}|\rho(r)|\right]^{1/3}. \tag{8}$$

Here $\rho(r)$ is the spherically averaged total electronic charge density, which is expressed as

$$\rho(r) = \frac{1}{4\pi}\sum_{\mu}\omega_{\mu}|\phi_{\mu}(r)|^2, \tag{9}$$

where ω_μ is the occupation number of the orbital μ, $\phi_\mu(r)$ is the electronic wave function of the orbital μ, and the summation is over all the AO's. In the case of chemical compounds, we replaced ω_μ for the valence electrons by P_μ obtained in Eq. (7), and by this procedure the atomtc potential $V(r)$ was modified through the variation in the exchange potential $V_{EX}(r)$.

For the metallic Tc, the electronic state has been estimated by the method of Watson *et al.*14) They showed that for the $3d$ transition metals, the core-electron state can be approximated by changing the number of $3d$ electrons in the free atoms. When the ground-state configuration is $(3d)^n(4s)^2$, the metallic configuration is approximately $(3d)^{n+1}(4s)$. If we extend this model to the $4d$ transition metal, the metallic Tc is expressed as $(4d)^6(5s)$. By the use of the same nonrelativistic HFS program, the SCF potential was calculated for the metallic Tc.

In the case of ^{99m}Tc, the relative change in the decay constant $\Delta\lambda/\lambda$ is equal to that in the internal conversion coefficient (ICC) $\Delta\alpha/\alpha$, because the conversion probability is quite large due to low transition energy and high multipolarity. Band *et al.*15) have shown that even for valence shells and for the high multipole-order transition the values of ICC are proportional to the electron density at the origin. Taking into account these facts, the relative change in the decay constant is written by

$$\frac{\Delta\lambda}{\lambda} \simeq \frac{\Delta|\phi(0)|^2}{|\phi(0)|^2}, \tag{10}$$

where $\phi(0)$ is the electronic wave function at the nucleus.

Owing to low transition energy of ^{99m}Tc, only electrons from M, N, and O shells can be ejected by the coversion process. Relative intensities of the M-subshell and the total N-shell ICC have been measured by two groups,16,17) and both results are in good agreement with each other and also with recent theoretical values.18,19) However, no experimental values for N-subshell ratios have been reported. In the present work, we used the tabulated values recently calculated by Rösel *et al.*19) and evaluated the relative

Table II. Internal Conversion Coefficients for 2.17-keV E3 Transition in ^{99m}Tc

Shell	Experimental		Theoretical			
	Ref. 16	Ref. 17	Ref. 20	Ref. 18	Ref. 19	Ref. 19 (Absolute)
M_1	<5		0.053		0.0449	2.48(+6)
M_2	41±10	56.4±2	50.2	56.6	56.7	3.13(+9)
M_3	100	100	100	100	100	5.53(+9)
M_4	50±10	47.6±2	71.9	47.0	20.5	1.13(+9)
M_5					31.5	1.74(+9)
N_1					0.0112	6.21(+5)
N_2					10.2	5.65(+8)
N_3					17.9	9.87(+8)
N_4					1.59	8.80(+7)
N_5					0.598	3.30(+7)
ΣN	30±7	28.6±5			30.30	

intensities for all M and N subshells at 2.17 keV. Contributions from the O shell are negligibly small. The relative intensities of ICC given in Ref. 19 are listed in Table II and compared with the experimental and other theoretical values.

Using the atomic potentials obtained above, we calculated the electron density at the nuclear surface for all M and N subshells and for metallic Tc, Tc_2S_7, and TcO_4^-. The Dirac equation was solved numerically for these electronic states in a central field. The nucleus is assumed to be a homogeneously charged drop whose radius is

$$R = 1.20 \times A^{1/3} \text{ fm}. \tag{11}$$

Inside the nucleus, the potential is given by

$$V(r) = (Z\alpha/2R)(r^2/R^2 - 3), \tag{12}$$

where Z is the atomic number and α is the fine structure constant.

Table III. Electron Density at Nuclear Surface in Tc Atoms in Three Different Chemical States

Shell	α_μ	$\lvert\phi(0)\rvert^2_{TcO_4^-}$	$\lvert\phi(0)\rvert^2_{Metal}$	$\lvert\phi(0)\rvert^2_{Tc_2S_7}$
M_1	0.0449	1.2034006(− 4)	1.2033938(− 5)	1.2033152(− 4)
M_2	56.7	2.2410858(− 6)	2.2407912(− 6)	2.2409625(− 6)
M_3	100	1.4425000(−10)	1.4423280(−10)	1.4420856(−10)
M_4	20.5	2.2336612(−13)	2.2331201(−13)	2.2323574(−13)
M_5	31.5	6.4181798(−18)	6.4166067(−18)	6.4140595(−18)
N_1	0.0112	2.1956075(− 5)	2.1819538(− 5)	2.1493070(− 5)
N_2	10.2	3.6442651(− 7)	3.6003729(− 7)	3.5521690(− 7)
N_3	17.9	2.3346684(−11)	2.3020577(−11)	2.2770886(−11)
N_4	1.59	2.3594002(−14)	1.9679906(−14)	2.3482417(−14)
N_5	0.598	6.7190409(−19)	5.5056875(−19)	6.7107273(−19)
$\sum_\mu \frac{\alpha_\mu \lvert\phi(0)\rvert^2_\mu}{\lvert\phi(0)\rvert^2_{\mu,Metal}}$		239.9022	239.0441	239.1193

Outside the nucleus, the potential is equal to the atomic potential calculated above. The numerical method to solve the Dirac equation is similar to that in Ref. 21. The calculated values of $|\phi(0)|^2$ for each M and N subshell in three different chemical environments are listed in Table III.

The relative change in the decay constant between two different chemical environments, A and B, is defined as

$$\frac{\Delta\lambda}{\lambda}=\frac{\sum_{\mu}\alpha_{\mu}|\phi^{B}(0)|_{\mu}^{2}/|\phi^{A}(0)|_{\mu}^{2}-\sum_{\mu}\alpha_{\mu}}{\sum_{\mu}\alpha_{\mu}}, \tag{13}$$

where $|\phi^{A}(0)|_{\mu}^{2}$ and $|\phi^{B}(0)|_{\mu}^{2}$ are the density of the μ-shell electron at the nuclear surface in A and B, and α_{μ} is the μ-shell ICC. The $\Delta\lambda/\lambda$ values have been calculated for two combinations; Tc_2S_7-TcO_4^- and Tc_2S_7-metallic Tc.

III. RESULTS AND DISCUSSION

Theoretical calculations have been performed in the manner described in the preceding section on the FACOM M-190 computer in the Data Processing Center of Kyoto University. The calculated results indicate that the large contribution to $\Delta\lambda/\lambda$ comes from $4d$-shell electrons, though the values of ICC for these shells are small, about 1% of total conversion probability. Morever, in general trend the decrease in the valence-electron density due to chemical bonding leads to increase the core-electron density at the nuclear surface. The latter fact yields a larger conversion probability for chemical compounds than for metallic Tc. These behaviors found here are consistent with that presented by Perlman and Emery.[22]

The numerical results obtained theoretically are listed in Table IV, where the experimental values are also given for comparisons. The calculated value for the Tc_2S_7-TcO_4^-

Table IV. Relative Differences($\Delta\lambda/\lambda\times10^4$) in the Decay Constant of ^{99m}Tc in Different Chemical Environments

Source pair	Experimental		Theoretical
	Refs. 3, 4	Ref. 5	Present
$\frac{\lambda(TcO_4^-)^{a}-\lambda(Tc_2S_7)}{\lambda(Tc_2S_7)}$	27.0±1.0		
$\frac{\lambda(Tc_2S_7)-\lambda(\text{metal})^{b}}{\lambda(Tc_2S_7)}$	3.1±1.2[c]		
$\frac{\lambda(TcO_4^-)^{d}-\lambda(Tc_2S_7)}{\lambda(Tc_2S_7)}$		31.8±0.7	32.7
$\frac{\lambda(Tc_2S_7)-\lambda(\text{metal})^{e}}{\lambda(\text{metal})}$		5.6±0.3	3.15

[a] $KTcO_4$.

[b] Electroplated on nickel and reduced in H_2 at 1000°C.

[c] In the abstract of Ref. 4, they give $\lambda(\text{metal})-\lambda(Tc_2S_7)=(3.1\pm1.2)\times10^{-4}\lambda(Tc_2S_7)$. But from their statements in Refs. 3 and 4, it is evident that the sign of the difference as measured by Bainbridge *et al.* is opposite, as referred in this Table.

[d] ϕ_4AsTcO_4.

[e] Eectrodesited on a Cu plated tungsten wire and reduced in H_2 at 800-1000°C.

pair is in excellent agreement with measured values, but for the Tc_2S_7-metallic Tc pair the theoretical value is about 2 times smaller than the experimental result.

The disagreement in the latter pair can be ascribed to the inadequency of the approximation used for the metallic Tc. The method of Watson *et al.*¹⁴⁾ is a good approximation to energy eigenvalues of the metallic states, but may not be appropriate for the wave functions.

In addition, considering many assumptions and approximations in the present calculations, it is difficult to discuss quantitatively the chemical effect on λ. The agreement found for the Tc_2S_7-TcO_4^- pair is probably fortuitous. Nevertheless, it may be said that qualitative agreements of the theoretical results presented here with the experiments, *i. e.*, $\lambda(TcO_4^-) > \lambda(Tc_2S_7) > \lambda$ (metallic Tc), suggest that the present simplification is to some extents effective for explanations of the chemical effect on λ, but more precise structural information is needed to refine the theoretical evaluation of the chemical effect.

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