Internal conversion of nuclear transition in the $^{235m}\text{U}@\text{C}_{60-n}X_n$ molecules and related compounds

Alexei M. Frolov

Department of Chemistry, University of Western Ontario, London K7L 3N6, Canada

(Dated: January 20, 2010)

Abstract

The internal conversion of nuclear transition in the $^{235}\text{U}$ atom is considered. The low-energy $\gamma$–quanta ($E_{\gamma} \approx 76.8$ eV) are emitted during the $E3$–transition from the excited state ($I = (\frac{1}{2})^+$) of the $^{235}\text{U}$ nucleus to its ground state ($I = (\frac{7}{2})^-$). The decay rate of this $^{235m}\text{U}$ isomer ($E \approx 76.8$ eV) noticeably depends upon the chemical composition and actual physical conditions (i.e. temperature $T$ and pressure $p$). By varying such a composition and physical conditions one can change the life-time of the $^{235m}\text{U}$ isomer to relatively large/small values. A specific attention is given to the fullerene molecules containing the central $^{235}\text{U}$ atom. It is shown that the decay rate $\lambda$ of the $^{235m}\text{U}$ isomer in the $^{235m}\text{U}@\text{C}_{60-n}X_n$ molecules and related compounds can differ significantly from the values obtained for isolated $^{235}\text{U}$ atoms. Some applications of this effect are considered.
As is well known the rate of nuclear reactions and processes is usually independent of the chemical background and physical conditions. In particular, the transition rate between two arbitrary nuclear states cannot depend upon the chemical environment and temperature (or pressure) of the considered experimental sample. However, in some cases the nuclear transition energies can be relatively small. If such an energy is comparable to the energy of corresponding atomic levels, then the nuclear transition can proceed by conversion of the emitted $\gamma$–quanta into electron shells of the considered atom (Akhiezer and Beresteskii (1965) [1]). Obviously, the most interesting case is the conversion of nuclear transition to the outer electron shells of atoms. In these cases one can change, in principle, the observed nuclear conversion rate by varying the chemical environment and/or physical conditions. Such a situation can be found in some heavy atoms, e.g., in the $^{235}$U atom.

This effect was already experimentally demonstrated for the $^{235m}$U-isomer (Mévergnies (1969), (1972), Zhudov et al (1979) [16], [17], [21]). The $^{235m}$U-isomer ($E \approx 76.8$ eV $\pm 0.5$ eV (Zhudov et al [21])) is extensively produced by $\alpha$-decay of $^{239}$Pu in the core of nuclear warheads and reactors. This isomer is the first excited state ($I = (\frac{1}{2})^+$) of the $^{235}$U nucleus which is only $\approx 76.8$ eV above its ground state ($I = (\frac{7}{2})^-$). The corresponding (nuclear) $E3$–transition to the ground state of the $^{235}$U nucleus (Grechukhin and Soldatov (1976) [6]) usually proceeds as an internal conversion of the nuclear transition to the outer electron shells (i.e. to the $5f_{5/2}, 5f_{7/2}, 6s_{1/2}, 6p_{1/2}, 6p_{3/2}, 6d_{3/2}, 6d_{5/2}, 7s_{1/2}$ shells) of the $^{235}$U atom. The half-life of the $^{235m}$U isomer is $\approx 26$ min (Zhudov et al (1979) [21]). In earlier experiments the nuclei of $^{235m}$U-isomer were implanted (Mévergnies (1969) [16]) into various metallic foils. The considered cases (Mévergnies (1969) [16]) included the Au, Pt, Cu, Ni, V foils. The decay rate $\lambda$ of the $^{235m}$U isomer was measured in each of these cases. The maximal deviation between the results obtained with different metals was found to be $\approx 5\%$ (Mévergnies (1969), (1972) [16], [17]).

The approximate theory of internal conversion of nuclear $\gamma$–quanta emitted during the $E3$–transition in the $^{235m}$U nucleus was developed in Grechukhin and Soldatov (1976) [6]. The basic idea which drastically simplifies calculation of the corresponding matrix element (Akhiiezer and Beresteskii (1965) [1]) is based on the fact that the proton orbit inside of the nucleus has significantly shorter radius than the corresponding electron orbits in the considered atom. In Grechukhin and Soldatov (1976) [6] the incident electron shells in the $U$ atom were described with the use of Hartree-Fock-Slater relativistic approach. In this
approach a model with a spherically symmetric, central potential is used to represent the electron-nucleus and direct electron-electron interaction. The exchange electron-electron interaction is replaced by an approximate (or effective) local, central potential. In the central potential approach the incident (or bound) electron state is designated by the \( n, j, \ell \) numbers, where \( n \) is the principal quantum number, \( \ell \) is the angular momentum and \( j \) represents the total momentum of the considered electron shell. For a given value of \( j \) we have \( \ell = j \pm \frac{1}{2} \). One of these \( \ell \)–values is even and the other is odd. Therefore, the known values of \( j \) and parity of the considered state uniquely determine \( \ell \). It was shown in Grechukhin and Soldatov (1976) \cite{6} that for the \( E_3 \)–transition of the \( ^{235}U \) nucleus from the isomer level with spin \( I_1 \) to the ground level with spin \( I_2 \) the partial conversion probability \((W)\) per one electron in the \( n_1j_1\ell_1 \) state takes the form

\[
W(E_3; I_1 \to I_2; n_1, \ell_1, j_1; \epsilon, \ell_2, j_2) = \frac{2I_2 + 1}{2I_1 + 1} \left\langle I_2 \mid \mid E_3 \mid | I_1 \right\rangle ^2 \cdot \left( \frac{R_0}{a_0} \right)^6 \cdot \frac{e^4 m_e}{\hbar^3} \cdot w_e(E3; n_1, \ell_1, j_1; \epsilon, \ell_2, j_2),
\]

where \( R_0 \approx 1.26A_1^4 \approx 7.775 \times 10^{-13} \text{ cm} \) is the nuclear \((^{235}U)\) radius, \( A = 235 \) is the total number of nucleons in the \( ^{235}U \) nucleus and \( a_0 = 5.29177249 \times 10^{-9} \text{ cm} \) is the Bohr radius. The Planck constant divided by \( 2\pi \) is designated in Eq.(1) by \( \hbar \), \( m_e \) is the electron mass and \( e \) is the electron charge. In fact, \( \frac{e^4 m_e}{\hbar^3} = 4.13413733 \times 10^{16} \text{ sec}^{-1} \) is the inverse atomic time (or basic atomic frequency in Hz). Also, in this formula \( w_e(E3; n_1, \ell_1, j_1; \epsilon, \ell_2, j_2) \) is the so-called electronic factor which is determined from relativistic atomic calculations (see below). In this study we shall assume that the central field approximation can be used to represent both the incident and final atomic states. The notation \( \left\langle I_2 \mid \mid E_3 \mid | I_1 \right\rangle \) in Eq.(1) stands for the dimensionless reduced matrix element of the nuclear \( E_3 \)–transition. This matrix element is of the form

\[
\left\langle I_2 \mid \mid E_3 \mid | I_1 \right\rangle = \frac{1}{C_{L_2M_2}^{I_2M_2}} \langle I_2M_2 \mid \sum_{i=1}^{A} q_i \left( \frac{r_i}{R_0} \right)^3 Y_{3M}(n_i) \mid I_1M_1 \rangle
\]

where \( C_{L_1M_1;LM}^{I_2M_2} \) is the corresponding Clebsch-Gordan coefficient, \( Y_{LM}(n) \) are the spherical harmonics. Also, in this equation \( R_0 \) is the radius of \( ^{235}U \) nucleus defined above, while \( r_i = | \mathbf{r}_i | \), where \( \mathbf{r}_i \) is the nucleon radius-vector \((i = 1, \ldots, A)\) in the nucleus. The \( q_i \) is the charge of nucleon, i.e., \( q_i = 1 \) for protons and \( q_i = 0 \) for neutrons. It is clear that only protons contribute to the sum in Eq.(2). In fact, the numerical value of the reduced nuclear matrix element \( \langle I_2 \mid \mid E_3 \mid | I_1 \rangle \) has been evaluated in earlier studies. In particular,
in Grechukhin and Soldatov (1976) it was shown that the numerical value for this matrix element is bounded between \( \approx 1.12 \cdot 10^{-2} \) and \( \approx 1.26 \cdot 10^{-2} \). Below, we shall assume that the \( \langle I_2 || E3 || I_1 \rangle \) matrix element is \( 1.20 \cdot 10^{-2} \).

Finally, the expression for the partial conversion probability takes the form

\[
W(E3; I_1 \rightarrow I_2; n_1, \ell_1, j_1; \epsilon_2, \ell_2, j_2) = 2.3955 \cdot 10^{-10} \cdot w_e(E3; n_1, \ell_1, j_1; \epsilon_2, \ell_2, j_2) \sec^{-1}.
\]

Thus, the original nuclear-atomic problem is reduced to the computation of a pure atomic matrix element \( w_e(E3; n_1, \ell_1, j_1; \epsilon_2, \ell_2, j_2) \) which includes only atomic (or molecular) wave functions (see below). In particular, for an isolated \(^{235}U\) atom the matrix element \( w_e(E3; n_1, \ell_1, j_1; \epsilon_2, \ell_2, j_2) \) takes the form

\[
w_e(EL; n_1, \ell_1, j_1; \epsilon_2, \ell_2, j_2) = \frac{8\pi}{p} \frac{2\ell_1 + 1}{(2L + 1)^2} \sum_{jj_2} (2j_2 + 1) | C_{\ell_20}^{\ell_10;L0} | R_h(L, \ell_2, j_1, \frac{1}{2}; \ell_1, j_2) |^2
\]

\[
(1 + \gamma_2) \int_0^{+\infty} r^{-(L+\frac{1}{2})} dr | g_{n_1,\ell_1,j_1}(r) g_{\epsilon_2,j_2}(pr) + \sqrt{\frac{\gamma_2 - 1}{\gamma_2 + 1}} f_{n_1,\ell_1,j_1}(r) f_{\epsilon_2,j_2}(pr) |^2,
\]

where \( p = | \mathbf{p} | \) is the total momentum of the outgoing (free) electron, while \( \gamma_2 = \frac{c_2}{mc^2} \) is the Lorentz \( \gamma \)-factor of this electron. Also, in this formula \( R_h(L, \ell_2, j_1, \frac{1}{2}; \ell_1, j_2) \) is the corresponding Racah function which is simply related to the Wigner 6-j symbol (see, e.g., Brink and Satchler [4]). The radial functions \( g_{n_1,\ell_1,j_1}(r) \) and \( f_{n_1,\ell_1,j_1}(r) \) are the large and small radial components of the bi-spinor wave function of the bound \( n_1, j_1, \ell_1 \)-state of the \(^{235}U\) atom. Analogously, the radial functions \( g_{\epsilon_2,j_2}(pr) \) and \( f_{\epsilon_2,j_2}(pr) \) are the large and small radial components of the bi-spinor wave function of the continuous atomic spectrum with energy \( \epsilon_2 \) and total momentum \( p \) (Akhiezer and Beresteskii (1965) [1]). Note that \( p \) is a scalar and \( \epsilon_2^2 = p^2c^2 + m_e^2c^4 \). In fact, in the present case \( L = 3 \). Therefore, in the case of \( s \)- and \( p \)-radial functions this radial integral, in general, contains singularities.

The decay rate constant \( \lambda(^{235m}U) \) of the \(^{235m}U\) isomer, Eq.(3), is the sum of all partial conversion probabilities for single-electron states. In the case of an isolated \(^{235}U\) atom the constant \( \lambda(^{235m}U) \) is written in the form

\[
\lambda(^{235m}U) = 2.3955 \cdot 10^{-10} \sum_{n_1,j_1,\ell_1} N(n_1, j_1, \ell_1) w_e(EL; n_1, \ell_1, j_1; \epsilon_2, \ell_2, j_2) \sec^{-1}, \quad (5)
\]

where the sum is taken over all electron states (orbitals) in which the conversion process is energetically allowed. Also, in this equation \( N(n_1, j_1, \ell_1) \) are the so-called occupation numbers of single-electron atomic states \( (n_1, j_1, \ell_1) \) (or orbitals). In general, by using a pulse
of laser radiation one can change the occupation numbers \( N(n_1, j_1, \ell_1) \) in the incident \(^{235m}U\) atom. The decay rate constant of the \(^{235m}U\) isomer will change correspondingly. This method can be used to measure the single-electron factors \( w_e(EL; n_1, \ell_1, j_1; \epsilon_2, \ell_2, j_2) \) experimentally. The theoretically predicted values for all contributing single-electron shells are \( w_e(6p_{1/2}) = 4.95 \times 10^5 \), \( w_e(6p_{3/2}) = 2.17 \times 10^5 \), \( w_e(6d_{5/2}) = 4.45 \times 10^4 \), \( w_e(6d_{3/2}) = 4.09 \times 10^4 \), \( w_e(5f_{5/2}) = 6.87 \times 10^2 \), \( w_e(6s_{1/2}) = 6.58 \times 10^2 \), \( w_e(5f_{7/2}) = 3.01 \times 10^2 \), \( w_e(7s_{1/2}) = 7.05 \times 10^1 \). These values have been obtained with the use of MOLFDIR package for relativistic quantum chemistry calculations (Visscher et al (1994) [19]) and they agree quite well with the corresponding \( w_e \) factors determined in Grechukhin and Soldatov (1976) [6]. These values indicate clearly that the electrons from \( 6p_{1/2}, 6p_{3/2}, 6d_{3/2} \) and \( 6d_{5/2} \) shells of the \(^{235}U\) atom are the main contributors to the \(^{235m}U\) decay rate constant. The decay rate constant \( \lambda(^{235m}U) \) computed with our \( w_e \) factors for the \( (6s_{1/2})^2(6p_{1/2})^2(6p_{3/2})^4(5f_{5/2})^3(6d_{5/2})^1(7s_{1/2})^2 \) electron configuration of the \(^{235m}U\) atom is \( \approx 2193.18 \text{ sec} = 36.55 \text{ min} \). This value exceeds the known experimental value of the \( \lambda(^{235m}U) \) constant (Zhudov et al (1979) [21]) by \( \approx 40 \% \).

Now, note that the same expression Eq. (5) can be used in those cases, when the \(^{235}U\) atom is bounded into a molecule or molecular structure. In such cases, however, the numbers \( N \) in Eq. (5) represent the occupation numbers of molecular orbitals. In the first approximation molecular orbitals can be considered as linear combinations of atomic orbitals including single-electron orbitals form the central \(^{235}U\) atom. Thus, in the case of a molecule which contains one \(^{235}U\) atom the last expression must be modified to the following form

\[
\lambda(^{235m}U) = 2.3955 \times 10^{-10} \sum_{n_1,j_1,\ell_1} N^{(M)}(n_1, j_1, \ell_1) \sum_{\epsilon_2,\ell_2,j_2:F} w_e^{(M)}(n_1, \ell_1, j_1; A; \epsilon_2, \ell_2, j_2; F) \\
= 2.3955 \times 10^{-10} \sum_{n_1,j_1,\ell_1} \left[ N(n_1, j_1, \ell_1) + \Delta N^{(M)}(n_1, j_1, \ell_1) \right] \sum_{\epsilon_2,\ell_2,j_2:F} \left[ w_e(n_1, \ell_1, j_1; \epsilon_2, \ell_2, j_2; F) + \Delta w_e^{(M)}(n_1, \ell_1, j_1; A; \epsilon_2, \ell_2, j_2; F) \right],
\]

where \( (n_f, \ell_f, j_f) \) is the final state of the uranium atom. Here \( N^{(M)}(n_1, j_1, \ell_1) \) is the occupation number of the corresponding atomic orbital in the \(^{235}U\) atom which is bounded into a larger molecular structure. For our present purposes it is important to note that for the closed shells of the \(^{235}U\) atom we always have \( N^{(M)}(n_1, j_1, \ell_1) < N(n_1, j_1, \ell_1) \), i.e., \( \Delta N(n_1, j_1, \ell_1) < 0 \). This means that the occupation numbers for the bounded uranium atom can be different from the occupation numbers of an isolated \(^{235}U\) atom. In general, only by varying the occupation numbers of the \( 6p_{1/2} \) and \( 6p_{3/2} \) orbitals in the \(^{235}U\) atom
one can change the $\lambda^{(235mU)}$ constant noticeably. The energy of the $(6p)_{\frac{1}{2}}$ electron in the uranium atom is $\approx 36.55$ eV, while the corresponding energies of $(6p)_{\frac{3}{2}}$ electron is $\approx 26.80$ eV. Therefore, a relatively large overlap between the $6p$ electrons of uranium atom and surrounding molecular orbitals can be expected in those cases when the considered molecule has a number of quasi-bound (or resonance) excited states with close energies $\approx 26 - 37$ eV. In fact, it is shown below that the energies of excited molecular states can be even $\approx 18 - 29$ eV. However, it is clear that in any case such a molecule must contain a relatively large number of atoms to avoid its instant fragmentation.

The expression for single-electron conversion factor $w_e^{(M)}(EL; n_1, \ell_1, j_1; A; \epsilon_2, \ell_2, j_2; F)$ in the case of a molecule with one central $^{235}U$ atom takes a very complex form. For instance, the indexes $A$ and $F$ which stand for the incident and final states of the considered molecule are essentially the multi-indexes. This means that $A$ and $F$ contain all rotational, vibrational, electronic and spin quantum numbers which are needed to represent uniformly the corresponding molecular state. Below, we shall assume that the incident molecular state is an excited molecular state and all molecular wave functions used below are normalized to unity. As we mentioned above our present main interest is related to the large molecules which contain one central uranium-235 atom.

An explicit expression for the $w_e^{(M)}(EL; n_1, \ell_1, j_1; A; \epsilon_2, \ell_2, j_2; F)$ factor in Eq.(6) can be found, e.g., in the case when the central $^{235}U$ atom is well separated from surrounding atoms in the molecule. In this case the cluster approximation can be used and expression for the additional $\Delta w_e^{(M)}(EL; n_1, \ell_1, j_1; A; \epsilon_2, \ell_2, j_2; F)$ factor takes the from

$$\Delta w_e^{(M)}(n_1, \ell_1, j_1; A; \epsilon_2, \ell_2, j_2; F) = b \left| \sum_{j=1}^{N} \langle \Psi_A(r_1, \ldots r_N) | B(r_j) | \Psi_F(r_1, \ldots r_N) \rangle \right|^2,$$

where $b$ is a positive constant, $r_j$ (where $j = 1, 2, \ldots, N$) are the electron coordinates in the considered molecule. Here $N$ is the total number of electrons in this molecule and $\Psi_A$ and $\Psi_F$ are the incident and final molecular wave functions. In the first approximation the operator $B(r_j)$ takes the following form

$$B(r_j) = \int_0^{\infty} g_{j_2\ell_2}(pr) g_{n_1\ell_1}(r)r^2 dr \oint \frac{1}{| \mathbf{r} - \mathbf{r}_j |} \Omega_{j_2\ell_2} M_2(n) \Omega_{j_1\ell_1} M_1(n) d\mathbf{n},$$

where $\mathbf{r}$ is the electron radius for the considered single-electron state (i.e. orbital) in the $^{235}U$ atom. The vector $\mathbf{n} = \frac{\mathbf{r}}{r}$ is the corresponding unit vector, while $\Omega_{j_i\ell_i} M_i(n)$ ($i = 1, 2$) are the ‘upper’ spinors which depend upon the angular variables $\mathbf{n}$. Also, in this equation...
\[ \gamma_2 = \frac{c^2}{m_\text{ee}} \] and \[ p^2 = \frac{\gamma^2}{\epsilon} - m_\text{e}^2c^2. \] Note that the small radial components \( f_{j_2 \ell_2}(pr) \), \( f_{n_1 j_1 \ell_1}(r) \) and corresponding angular spinors will contribute to the \( \Delta w_e^{(M)}(n_1, \ell_1, j_1; A; \epsilon_2, \ell_2, j_2; F) \) matrix element only in the next (higher-order) approximation upon the fine structure constant \( \alpha \approx 7.29735308 \cdot 10^{-3} \ll 1 \). In the higher order approximation, however, the operator \( B(r_j) \) takes significantly more complicated form, since now it must include the correction which correspond to the retarded interaction between charged particles.

Note that the molecular conversion of nuclear transition represented by Eq.(6) proceeds with the use of an intermediate atom (the \( ^{235}\text{U} \) atom in our case). The direct molecular conversion of nuclear \( \gamma \)-quanta is negligibly small, since the averaged molecular radius \( R_M \) in large molecules \( (R_M \approx 10a_0) \) is significantly larger than the nuclear radius \( R_0 \). This produces an additional factor of \( \sim 10^{-6} - 10^{-8} \) in Eq.(1). In contrast with this, the internal molecular conversion of nuclear transition with the use of intermediate \( ^{235}\text{U} \) atom has significantly larger probability and can be observed experimentally. Moreover, for some molecular structures the rate of molecular conversion of nuclear transition can be different from the rate of pure atomic conversion in the \( ^{235}\text{U} \) atom. This means a noticeable change in the decay rate constant \( \lambda(^{235\text{m}}\text{U}) \) of the \( ^{235\text{m}}\text{U} \) isomer, Eq.(6), in some molecules.

In general, the absorption of any significant amount of energy \( \approx 20 - 36 \text{ eV} \) in the considered case means, the partial (or complete) dissociation of any few-atom molecule. In fact, below we shall consider the molecular excitations with energies \( \approx 77 \text{ eV} \) and even \( 100 \text{ eV} \). The dissociation usually proceeds as a fragmentation of the incident molecule into a number of fragments. Another possible way is the ionization (or photoionization) of the incident molecule. In many cases, both molecular fragmentation and photoionization occur together. In general, however, the molecular bond strengths are \( \approx 4.5 \text{ eV} \), while the photoionization of molecules requires \( \approx 15 \text{ eV} \). Moreover, the matrix element which describes the photoionization contains the fine structure constant \( \alpha \approx 7.29735308 \cdot 10^{-3} \ll 1 \). Therefore, the molecular photoionization usually has smaller probability than the molecular fragmentation. Below, our main interest is related to the consideration of stable molecules in the incident and final state. In this case, one finds that the minimal number \( N_{\text{min}} \) of atoms in such a molecule must exceed \( N_{\text{min}} \approx 77/4.0 \approx 19 \). In reality, the molecular fragmentation starts at smaller energies \( \approx 2 \text{ eV} \) per atom, see below). This means that \( N_{\text{min}} \approx 38 - 40 \), i.e. the molecules which are of interest for our present purposes must contain at least 40 - 45 atoms. In the case of \( \approx 100 \text{ eV} \) molecular excitation the number of atoms per molecule
must be $\approx 50 - 55$.

To change the rate of internal conversion of low-energy nuclear $\gamma$-quanta we propose to use the molecular structures based on fullerenes $C_{60}, C_{84}, C_{100}$, etc. The corresponding molecular structures have the following general formula $^{235m}U@C_n$, where $n \geq 60$. Note that the fullerenes recently attracted a significant experimental attention (see, e.g., Handschuh et al (1995), Joachim et al (2000) and references therein). In particular, the fullerenes were suggested for numerous applications in the field of molecular electronics (Park et al [18]). It is shown below that fullerenes are also of certain interest for applied nuclear physics.

For our present purposes it is important to note that the instant fragmentation of fullerenes and related molecular structures starts (see, e.g., Mowrey et al (1991) when the critical energy per carbon atom (i.e., $E_{\text{crit}}/n$, where $n \geq 60$) exceed $2.7 \ eV$. If $E_{\text{crit}}/n \geq 3.5 \ eV$, then the instant fragmentation proceeds rapidly (Mowrey et al (1991)). The average bond strengths in fullerenes are of the order $4.5 - 5 \ eV$. From here one finds that the instant fragmentation of the $C_{60}$ molecule can start, if the critical energy $E_{\text{crit}} \geq 2.7 \times 60 \approx 162 \ eV$. In the present case, the maximal excitation energy $E$ is $\leq 77 \ eV$. Therefore, the effective excitation energy per each carbon atom ($\approx 1.3 \ eV$) is approximately twice smaller than $2.7 \ eV$. In fact, for the $C_{60}$ molecule the bulk of the incident excitation energy is distributed among the 60 atoms in the $C_{60}$ molecule. Moreover, if the $C_{60}$ molecules are associated (or implanted) in some larger molecular clusters, e.g., carbon nanotubes (see, e.g., Monthioux (2002)), then the incident molecular excitation (e.g., $77 \ eV$ and $100 \ eV$ excitations) can be transferred almost instantly to/from some distant molecules. In particular, below we shall assume the incident state of the fullerene $C_{60}$ molecule in an excited state, while the central $^{235}U$ atom in its ground state. The same consideration can be applied to any fullerene molecule which contain the central uranium atom $^{235m}U@C_n$ where $n = 84, 100, 128$, etc.

In addition to the regular fullerene molecules, one can also consider the similar $^{235m}U@C_{60-\text{m}}X_m$ molecular structures, where $X$ are the non-carbon atoms (e.g., boron, nitrogen or hydrogen atoms) and $m \leq 12$ (Guo et al (1991), Hummelen et al (1995), Hultman et al (2001) and references therein). In general, the $C_{60-\text{m}}X_m$ molecules are slightly less stable than the pure fullerene molecules $C_{60}$. The molecular bond strengths usually decrease by $\approx 0.30 \ eV$ per substituted atom. In the case of nitrogen such a deviation can be even $\approx 0.60 \ eV$ per each additional nitrogen atom (Hummelen et al (1995), Hultman et al (2001)).
However, in any case the considered $C_{60-m}X_m$ molecules are stable and can be used for our present purposes. Moreover, currently, the $^{235m}U@C_{60-m}X_m$ molecular structures are the most promising systems for the future experiments to study the internal molecular conversion of low-energy nuclear transition. Indeed, by varying the number of substituted atoms in the $^{235m}U@C_{60-m}X_m$ molecules one can change the occupation numbers $N$ and molecular matrix element $w_e^{(M)}(n_1, \ell_1, j_1, A; \epsilon_2, \ell_2, j_2; F)$ in Eq.(6). In some $^{235m}U@C_{60-m}X_m$ molecules, the resonance conditions between the incident and final states can be obeyed almost exactly. In contrast with this, there is no sense to apply the higher fullerenes $^{235m}U@C_n$, where $n \geq 128$, in the experiments related to the internal molecular conversion of low-energy nuclear transition. This follows from the fact that the effective uranium-carbon distance in fullerenes decreases with $n$. The molecular matrix elements $w_e^{(M)}(n_1, \ell_1, j_1, A; \epsilon_2, \ell_2, j_2, F)$ for large $n$ ($n \geq 128$) almost coincides with the corresponding atomic ($^{235}U$) matrix element Eq.(5). The presence of distant carbon atoms in the $^{235m}U@C_n$ molecule does not play any noticeable role for $n \geq 200$.

In this study our analysis was restricted to the $^{235m}U@C_{60}$ molecule only. Moreover, it was assumed that the outer electrons in the incident $^{235}U$ atom form the $(6s_\frac{1}{2})^2(6p_\frac{1}{2})^2(6p_\frac{3}{2})^4(5f_\frac{5}{2})^3(6d_\frac{3}{2})^1(7s_\frac{1}{2})^2$ electron configuration. Note that the $(5f)^3(6d)^1(7s)^2$ outer electron configuration (term $^5L_{J=6}$, odd parity) is usually considered (see, e.g., Avery (2003) [2]) as the valency configuration (i.e. the ground state) of the uranium atom. The first excited state (term $^5K_{J=5}$, odd parity) of the uranium atom has relatively small excitation energy $\Delta \approx 0.077$ eV. In general, the valency configuration changes drastically when uranium atom is bounded into different molecules or implanted in various metallic alloys. Nevertheless, it was assumed in earlier works (Mévergnies (1972), Grechukhin and Soldatov (1976) [17, 6]) that the $(6s_\frac{1}{2})^2(6p_\frac{3}{2})^2(6p_\frac{1}{2})^4$ configuration of deep-lying 6-shell electrons does not change when uranium atoms form molecules (or implanted in metals). In this study we also considered a number of cases when only the valency configuration was varied. Briefly, our results for such cases can be described as follows. By varying the population of the $6d$–orbitals one can change (decrease) the decay rate constant $\lambda(^{235m}U)$ only by 3%. Analogous variation for the $7s$ electrons produces significantly smaller effect. For the $5f$ electrons the direct contribution to the decay rate constant is less than 1%. On the other hand, the $5f$ electrons penetrate some inner-lying electron shells of the uranium atom. Their interaction with the $(6p_\frac{1}{2})^2$ and $(6p_\frac{3}{2})^4$ electron shells can change, in principle, the
occupation numbers of these two 6p orbitals. In general, the decay rate constant \( \lambda^{(235mU)} \) increases drastically, when the population of 6p electron orbitals changes (decreases).

The idea to use the 5f electron shells in order to change the occupation numbers of the \((6p_{\frac{1}{2}})^2\) and \((6p_{\frac{3}{2}})^4\) electron shells can be extremely productive for the \(^{235mU}@C_{60}\) molecule and other similar molecules. Indeed, the excitation of one electron from the 6p shell to 5f shell decreases the constant \( \lambda^{(235mU)} \) by \( \approx 21\% \) in the case of the \((6p_{\frac{1}{2}})\) shell and by \( \approx 9.5\% \) for the \((6p_{\frac{3}{2}})\) shell. The half-life of the \(^{235mU}\) isomer increases correspondingly. In the case of two-electron excitation from the same shells the half-life of \(^{235mU}\) isomer increase up to \( \approx 40 \) minutes and \( \approx 31 \) minutes, respectively. In any case, this effect can be observed and measured experimentally. Note that the excitation transitions from the 6p—shell to the 6d—shells of the \(U\) atom are also possible, but they are less likely.

It is interesting to consider an opposite process, i.e. the nuclear excitation of the \(^{235}U\) nucleus by using molecular excitations in various large molecules. Analysis of the energy level structure in the uranium atom shows that this process can proceed only with the use of \((5d_{\frac{1}{2}})\) and \((5d_{\frac{3}{2}})\) electrons in the uranium atom. The corresponding (single-electron) energies of these electron shells are \( \approx 109.9857 \) eV and \( \approx 118.41311 \) eV, respectively. Such an excitation can still be accumulated in the \(C_{60-n}X_n\) molecule without producing its instant destruction. The energies of the \((5p_{\frac{3}{2}})\) and \((5p_{\frac{1}{2}})\) electron shells in the uranium atom are significantly higher (\( \approx 220.2218 \) eV and \( \approx 275.5916 \) eV, respectively). Therefore, the 5p—, 5s— and other internal electron shells of the uranium atom are of less interest for the considered applications. The transition of molecular excitation to the uranium nucleus can proceed in a following way. First, a vacancy is formed in the 5d—electron shell of uranium atom. The 6d—electron is moved to the 5f—, 6d—, 7p—, etc electron shells or to the continuous spectra. This step requires \( \approx 100-120\) eV of energy. On the second step this 5d—vacancy is filled by an electron from outer electron shells, e.g., from the \(6p_{\frac{1}{2}}, 6p_{\frac{3}{2}}, 5f_{\frac{1}{2}}, 6d_{\frac{1}{2}}\) or \(7s_{\frac{1}{2}}\) shells. In some cases, some part (\( \approx 77\) eV) of the energy released during this step can be used to form the excited \(^{235mU}\) nucleus. The rest of the energy can be either emitted as a radiation quanta, or imparted to the ejection of an electron from one of the outer electron shells without any photons being produced in the process (Auger effect combined with the nuclear excitation). In particular, the case when such a vacancy has formed in the \(6p_{\frac{3}{2}}\) electron shell is of specific interest. Currently, we evaluate the total probability of nuclear excitation (i.e. the probability of inverse internal conversion) as \( \approx 1\% \). This means that only 1 of 100
vacancies formed in the 5d–shells of the uranium-235 atoms will produce the corresponding nuclear excitation. Unfortunately, in this study we cannot present more detailed description of this process. Moreover, our current understanding of the atom-molecular interaction in the $^{235m}U@C_{60-n}X_n$ molecule and related compounds is far from complete. In the future, we are planning to apply more accurate methods developed recently for relativistic calculations of some complex molecules (Bagus et al (2000), Graaf et al (1998) [3], [5]). The consideration of atomic part of the problem (i.e. the description of $^{235}U$ atom) must be also improved. Nevertheless, after some improvements we hope to present a more accurate picture of the internal conversion of nuclear transition in the $^{235m}U@C_{60-n}X_n$ molecules.

In conclusion, let us discuss some applications of the considered phenomena. First, note that such a low-lying excited state ($\approx 77$ eV) can be found only in the $^{235}U$ nucleus. Analogous excited states in nuclei of other uranium isotopes have significantly larger energies. Therefore, the existence of the considered low-lying excited state in the $^{235}U$ nucleus can be used to separate the $^{235}U$ isotope from mixtures containing various uranium isotopes, e.g., the $^{233}U$, $^{234}U$, $^{236}U$ and $^{238}U$ isotopes. In fact, nowadays the separation of uranium isotopes is not an actual problem. Note, however, that the internal conversion of low-energy nuclear $\gamma$–quanta can be observed in some other fissionable elements. If the nuclear isomers with relatively small transition energies ($E \leq 150$ eV) do exist in the fissionable $^{247}Cm$ and $^{251}Cf$ nuclei, then it can be used to separate these two isotopes. In turn, the industrial separation of these two isotopes will be extremely beneficial for the future development of nuclear industry and weaponry.

The second and very interesting application is related to a possibility to control the neutron criticality (Weinberg and Wigner (1958) [20]) of fissionable materials by changing the population of two nuclear states (ground and considered low-lying excited states) in the $^{235}U$ nuclei. To discuss this effect we shall use the method which is based on the time-dependent diffusion model in fissionable materials (Weinberg and Wigner (1958) [20]). In this model the neutron propagation is given by the simple diffusion equation, which contains corrections for: (1) the absorption of neutrons by the nuclei in the medium, and (2) the production of neutrons by the fissions of fissionable nuclei. Both of these quantities are linear in the neutron flux $\Phi (\Phi = n \cdot v$, where $n$ is the neutron density and $v$ is the mean neutron velocity). Therefore, their sum can be written as one term and one-velocity
The diffusion equation takes the following form

$$\frac{1}{\nu} \frac{\partial \Phi}{\partial t} = \nabla (a^2 \nabla \Phi) + \beta \Phi \quad ,$$  

(9)

where the parameter $a^2$ (the so-called "diffusion coefficient") is

$$a^2 = \frac{A}{\rho N_A (\sigma_f + \sigma_c + \sigma_p) (1 - \cos \psi)} \approx \frac{A}{\rho N_A \sigma_t (1 - \frac{2}{3A})} \quad ,$$  

(10)

where $\sigma_f$ is the microscopic fission cross-section for the considered element and $\sigma_c$ is the microscopic neutron absorption cross-section. In fact, $\sigma_c$ means the so-called non-productive neutron capture cross-section. $\sigma_p$ is the macroscopic scattering cross-section, and $\sigma_t$ is the total neutron cross-section. Also, in this equation $\rho$ is the macroscopic density and $N_A = 6.0221367 \cdot 10^{23}$ is the Avogadro number, while $\cos \psi \approx \frac{2}{3A}$ is the so-called average cosine of neutron scattering (Weinberg and Wigner (1958) [20]). The parameter $\beta$ in Eq.(9) takes the following, well known (Weinberg and Wigner (1958) [20]) form

$$\beta = \frac{\rho N_A}{A} \left( (\nu - 1)\sigma_f - \sigma_c \right) \quad ,$$  

(11)

where the parameter $\nu = \nu(E)$ is the number of neutrons released per one fission, which is produced by a neutron with the energy $E$. The energy dependence of $\nu(E)$ is approximated by the following linear expression (Henkel (1964) [9]) $\nu(E) = \nu_0 + \alpha E$, where $\nu_0$ is the number neutrons released per fission with the thermal neutrons, and $E$ is the energy of the initial neutron (in $MeV$). For the uranium-235 we have $\nu_0 \approx 2.432$ and $\alpha \approx 0.100$ (Hoffman and Hoffman (1974) [10]).

In the case when $\beta > 0$ (i.e. $\nu \sigma_f > \sigma_f + \sigma_c$, or $\eta = \frac{\nu \sigma_f}{\sigma_f + \sigma_c} > 1$) the intensity of chain reaction will increase. This corresponds to the supercritical fissionable system. For binary mixture of the $^{235}U$ and $^{235m}U$ nuclei we can write $\sigma_f = x \sigma_f^{(m)} + (1 - x) \sigma_f$ and $\sigma_c = x \sigma_c^{(m)} + (1 - x) \sigma_c$, where $x$ is the isomer concentration, $\sigma_f^{(m)}$ and $\sigma_c^{(m)}$ are the corresponding neutron cross-sections of the $^{235m}U$ nucleus, while $\sigma_f$ and $\sigma_c$ are the neutron cross-sections of the $^{235}U$ nucleus in its ground ($\frac{7}{2}^-$) state. If there is a way to control the $^{235m}U$ isomer concentration $x(t)$, then it can be used to transform the fissionable mixture to a supercritical state (or vice versa to an undercritical state). There are a number of other applications which are based on internal convergence of low-energy nuclear transition in the $^{235m}U$ nuclei. The reversibility of such a conversion in the fullerene-based molecular structures which contain the $^{235}U$ atoms allows us to consider a significantly larger number
of applications. For instance, by using low-energy molecular excitations one can produce, in principle, the nuclear pumping in the $^{235}U$ sample. This means that the nuclear properties of such a sample can be changed in the result of molecular excitations. In conclusion, it should be mentioned that the considered molecular conversion of nuclear low-energy nuclear transition in the fullerene-based $^{235m}U@C_n$ molecules and related compounds $^{235m}U@C_{60-n}X_n$ warrants further theoretical and experimental study. In fact, some other large molecules which contain $^{235}U$ atoms can also be considered. Hopefully, this work will stimulate further experimental activity in studying of this very interesting phenomenon. If someone is interested in performing experiments described above, please, let me know by e-mail.

Acknowledgment

It is a pleasure to thank Professor Ria Broer (Groningen, The Netherlands) for permission to use the MOLFDIR computational package.

[1] Akhiezer, A.I., Berestetskii, V.B., Quantum Electrodynamics, (Interscience, New York, (1965)), Chp. VI.
[2] Avery J., Electronic Structure of Atoms (in: Handbook of Molecular Physics and Quantum Chemistry, Wiley, New York, 2003), 1, Chp. 17.
[3] Bagus, P.S., Broer, R., De Jong, W.A., Nieuwoort, W.C., Parmigiani F., Sangaleti, L., Atomic many-body effects for the p-shell photoelectron spectra of transition metals, Phys. Rev. Lett. 84, 2259 (2000).
[4] Brink, D.M., Satchler, G.R., Angular Momentum (2nd ed., Clarendon Press, Oxford, 1968).
[5] Graaf, C., De Jong, W.A., Broer, R., Nieuwoort, W.C., Theoretical study of the crystal field excitations in CoO, Chem. Phys. 237, 59 (1998).
[6] Grechukhin, D.P., Soldatov, A.A., Conversion E3 transition from the isomeric state of $^{235}U$ (73 eV), Yad. Fiz. 23, 273 (1976) [Sov. J. Nucl. Phys. 23, 143 (1976)].
[7] Guo, T., Jin, C.M., Smalley, R.E., Doping bucky: formation and properties of boron-doped buckminsterfullerene, J. Phys. Chem. 95, 4948 (1991).
[8] Handschuh, H., Gantefor, G., Kessler, B., Bechthold, P.S., Eberhardt, W., Stable configurations of carbon cluster: chain, rings and fullerenes, Phys. Rev. Lett. 74, 1095 (1995).
[9] Henkel, R.L., Fission by Fast Neutrons, in: Fast Neutrons Physics, Part II, (Wiley, New York, 1964) p. 2001 and references therein.

[10] Hoffman, D.C., Hoffman, M.M., Post-Fission Phenomena, Ann. Rev. Nucl. Sci. 24, 151 (1974) and references therein.

[11] Hultman L., et al, Cross-linked nano-onions of carbon nitride in the solid phase: existence of a novel $C_{48}N_{12}$ aza-fullerene, Phys. Rev. Lett. 87, 225503 (2001).

[12] Hummelen, J.C., Knight, B., Pavlovich, J., Gonzales, R., Wuld, F., Isolation of the hetero-fullerene $C_{50}N$ as its dimer, Science 269, 1554 (1995).

[13] Joachim, C., Gimzewski, J.K., Aviram, A., Electronics using hybrid-molecular and monomolecular devices, Nature (London) 408, 541 (2000).

[14] Monthioux, M., Filling single-wall carbon nanotubes, Carbon 40, 1809 (2002).

[15] Mowrey, R.C., Brenner, D.W., Dunlap, B.I., Mintminre J.W., White, C.T., Simulations of $C_{60}$ collisions with hydrogen-terminated diamond{111} surface, J. Phys. Chem. 95, 7138 (1991).

[16] Néve de Mévergnies, M., Chemical effects on the half-life of $U^{235m}$, Phys. Rev. Lett. 23, 422 (1969).

[17] Néve de Mévergnies, M., Perturbation of the $^{235}U$ decay rate by implementation in transition metal, Phys. Rev. Lett. 29, 1188 (1972).

[18] Park, H., Park, J., Kim, A.K.L., Anderson, E.H., Alivisatos, A.P., McEuen, P.L., Nanochemical oscillations in a single-$C_{60}$ transistor, Nature (London), 407, 57 (2000).

[19] Visscher, L., Visser, O., Aerts, P.J.C., Merenga, H., Nieuwoort, W.C., Relativistic Quantum Chemistry the MOLFDIR program package, Comp. Phys. Commun. 81, 120 (1994).

[20] Weinberg, A.W., Wigner, E.P., The Physical Theory of Neutron Chain Reactors (The University of Chicago Press, Chicago, 1958).

[21] Zhudov, V.I., Zelenkov, A.G., Kulakov, V.M., Mostovoi, V.I., Differential spectrum of the conversion electrons and the excitation energy of $(1/2^+)$-uranium-235 isomer, Pis’ma Zh. Eksp. Teor. Fiz. 30, 549 (1979) [JETP Letters 30, 516 (1979)].