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## ON PROBABILITIES OF THE VIBRATION-NUCLEAR TRANSITIONS IN SPECTRUM OF THE RuO<sub>4</sub> MOLECULE

There are firstly presented theoretical data on the vibration-nuclear transition probabilities in a case of the emission and absorption spectrum of the nucleus of ruthenium <sup>186</sup>Re ( $E_{\gamma}^{(0)} = 186.7$  keV) in the molecule of RuO<sub>4</sub>, estimated on the basis of consistent quantum-mechanical approach to cooperative electron- $\gamma$ -nuclear spectra (a set of the vibration-rotational satellites in a spectrum of molecule) of multiatomic molecules.

From physical viewpoint it is obvious that any alteration of the molecular state must be manifested in the quantum transitions, for example, in a spectrum of the  $\gamma$ -radiation of a nucleus (see for example [1-22]). In result of the gamma nuclear transition in a nucleus of a molecule there is arisen a set of the electron-vibration-rotation satellites, which are due to an alteration of the state of the molecular system interacting with photon. The known example is the Szilard-Chalmers effect which results to molecular dissociation because of the recoil during radiating gamma quantum with large energy (c.f. [1-5]).

In series of works [11-22] it has been carried out detailed studying the co-operative dynamical phenomena due the interaction between atoms, ions, molecule electron shells and nuclei nucleons. There have been developed a few advanced approaches to description of a new class of dynamical laser-electron-nuclear effects in molecular spectroscopy, in particular, a nuclear gamma-emission or absorption spectrum of a molecule.

A consistent quantum-mechanical approach to calculation of the electron-nuclear g transition spectra (set of vibration-rotational satellites in molecule) of a nucleus in the multiatomic molecules has been earlier proposed [13,14] and generalizes the well known approach by Letokhov-Minogin [8]. Earlier there were have been obtained

estimates and calculations of the vibration-nuclear transition probabilities in a case of the emission and absorption spectrum of nucleus <sup>191</sup>Ir ( $E_{\gamma}^{(0)} = 82$  keV) in the molecule of IrO<sub>4</sub>, <sup>188</sup>Os ( $E_{\gamma}^{(0)} = 155$  keV) in OsO<sub>4</sub> and other molecules were listed.

In this paper there are firstly presented theoretical data on the vibration-nuclear transition probabilities in a case of the emission and absorption spectrum of the nucleus of ruthenium <sup>97</sup>Ru in the molecule of RuO<sub>4</sub>, estimated on the basis of the simplified version [18,19] of the consistent quantum-mechanical approach to cooperative electron-g-nuclear spectra (a set of the vibration-rotational satellites in a spectrum of molecule) of multiatomic molecules.

As the method of computing is earlier presented in details, here we consider only by the key topics following to Ref. [18] The aim is to compute parameters of the gamma transitions (a probability of transition) or spectrum of the gamma satellites because of changing the electron-vibration-rotational states of the multi-atomic molecules under gamma quantum radiation (absorption). Here it is considered a case of the five-atomic molecules (of XY<sub>4</sub> type; T<sub>d</sub>).

Hamiltonian of interaction of the gamma radiation with a system of nucleons for the first nucleus can be expressed through the co-ordinates of nucleons  $r_n'$  in a system of the mass centre of the one nucleus [14,18]:

$$H(r_n) = H(r_n') \exp(-k_\gamma u) \quad (1)$$

where  $k_\gamma$  is a wave vector of the gamma quantum;  $u$  is the shift vector from equality state (coinciding with molecule mass centre) in system of co-ordinates in the space. The matrix element for transition from the initial state "a" to the final state "b" is presented as usually:

$$\langle \Psi_b^* | H | \Psi_a \rangle \bullet \langle \Psi_b^* | \hat{a}^{-k_\gamma u} | \Psi_a \rangle \quad (2)$$

where a and b is a set of quantum numbers, which define the vibrational and rotational states before and after interaction (with gamma- quantum). The first multiplier in eq. (2) is defined by the gamma transition of nucleus and is not dependent upon the internal structure of molecule in a good approximation. The second multiplier is the matrix element of transition of the molecule from the initial state "a" to the final state "b":

$$M_b \approx \Psi_b^*(r_e) | \Psi_a(r_e) \rangle \bullet \langle \Psi_b^*(R_1, R_2) | e^{-k_\gamma R_1} | \Psi_a(R_1, R_2) \rangle \quad (3)$$

The expression (3) gives a general formula for calculating the probability of changing the internal state of molecule during absorption or emitting g quantum by a nucleus. It determines an intensity of the corresponding g-satellites. Their positions are fully determined as follows:

$$E_\gamma = E_\gamma^0 \pm R + \hbar k_\gamma v \pm (E_b - E_a) \quad (4a)$$

Here  $M$  is the molecule mass,  $v$  is a velocity of molecule before interaction of nucleus with g quantum;  $E_a$  and  $E_b$  are the energies of the molecule before and after interaction;  $E_g$  is an energy of nuclear transition;  $R_{om}$  is an energy of recoil:

$$R_{om} = [(E_g^{(0)})^2 / 2Mc^2]. \quad (4b)$$

Obviously only single non-generated normal vibration (vibration quantum  $\hbar\omega$ ) is excited and initially a molecule is on the vibrational level  $v_a = 0$ . If denote a probability of the excitation as  $P(v_b, v_a)$  and use expression for shift  $u$  of the g-

active nucleus through the normal co-ordinates, then an averaged energy for excitation of the single normal vibration is as follows [8,14,18]:

$$\begin{aligned} \bar{E}_{\text{vib}} &= \sum_{v=0}^{\infty} \hbar\omega(v + 1/2) \bar{P}(v,0) - \hbar\omega/2 = \\ &= \sum_{v=0}^{\infty} \hbar\omega(v + 1/2) P(v,0) - \hbar\omega/2 = \\ &= \sum_{v=0}^{\infty} \hbar\omega(v + 1/2) \frac{z^v}{v!} e^{-z} - \frac{\hbar\omega}{2} = \frac{1}{2} R \left( \frac{M-m}{m} \right), \quad (5) \end{aligned}$$

where

$$z = (R/\hbar\omega) [M - m/m] \cos^2 \vartheta,$$

and  $m$  is the mass of g-active nucleus,  $\vartheta$  is an angle between nucleus shift vector and wave vector of g-quantum and line in  $\bar{E}_{\text{vib}}$  means averaging on orientations of molecule (or on angles  $\vartheta$ ). To estimate an averaged energy for excitation of the molecule rotation, one must not miss the molecule vibrations as they provide non-zeroth momentum  $L = k_\gamma u \sin \vartheta$ , which is transferred to a molecule by g-quantum. In supposing that a nucleus is only in the single non-generated normal vibration and vibrational state of a molecule is not changed  $v_a = v_b = 0$ , one could evaluate an averaged energy for excitation of the molecule rotations as follows:

$$\begin{aligned} \bar{E}_{\text{rot}} &= \langle B^2 \rangle = B_\gamma^2 \langle u^2 \rangle \overline{\sin^2 \vartheta} = \\ &= 1/2 R(B/\hbar\omega) [(M - m)/m] \quad (6) \end{aligned}$$

As for multi-atomic molecules it is typical  $B/\hbar\omega \sim 10^{-4} - 10^{-2}$ , so one could miss the molecule rotations and consider g-spectrum of a nucleus in the molecule mass centre as a spectrum of the vibration-nuclear transitions.

A shift  $u$  of the g-active nucleus can be expressed through the normal co-ordinates  $Q_{s\sigma}$  of a molecule:

$$u = \frac{1}{\sqrt{m}} \sum_{s\sigma} b_{s\sigma} Q_{s\sigma} \quad (7)$$

where  $m$  is a mass of the g- active nucleus; components of the vector  $b_{s\sigma}$  of nucleus shift due to the F-component of "s" normal vibration of a

molecule are the elements of matrix  $b$  [2]; it realizes the orthogonal transformation of the normal co-ordinates matrix  $Q$  to matrix of masses of the weighted Cartesian components of the molecule nuclei shifts  $q$ .

According to eq.(1), the matrix element can be written as multiplying the matrix elements on molecule normal vibration, which takes contribution to a shift of the  $g$ - active nucleus:

$$M(b, a) = \prod_s \left\langle v_s^b \left| \prod_{\sigma} \exp(-k_{\gamma} b_{s\sigma} Q_{s\sigma} / \sqrt{m}) v_s^a \right. \right\rangle. \quad (8)$$

It is obvious that missing molecular rotations means missing the rotations which are connected with the degenerated vibrations. Usually wave functions of a molecule can be written for non-degenerated vibration as:

$$|v_s\rangle = \Phi_{\mathbf{v}}(Q_s), \quad (9)$$

for double degenerated vibration in the form:

$$|v_s\rangle = (v_s + 1)^{-1/2} \sum_{\mathbf{v}} \Phi_{v_{s\sigma_1}}(Q_{s\sigma_1}) \Phi_{v_{s\sigma_2}}(Q_{s\sigma_2}) \quad (10)$$

(where  $v_{s\sigma_1} + v_{s\sigma_2} = v_s$ ) and for triple degenerated vibration as follows:

$$|v_s\rangle = \left( \frac{2}{(v_s + 1)(v_s + 2)} \right)^{1/2} \times \sum_{\mathbf{v}} \Phi_{v_{s\sigma_1}}(Q_{s\sigma_1}) \Phi_{v_{s\sigma_2}}(Q_{s\sigma_2}) \Phi_{v_{s\sigma_3}}(Q_{s\sigma_3}) \quad (11)$$

where

$$v_{s\sigma_1} + v_{s\sigma_2} + v_{s\sigma_3} = v_s.$$

In the simple approximation function  $\Phi_{v_{s\sigma}}(Q_{s\sigma})$  can be chosen in a form of the linear harmonic oscillator one. More exact calculating requires a numerical determination of these functions. Taking directly the wave functions  $|v_s^a\rangle$  and  $|v_s^b\rangle$ , calculating the matrix element (8) is reduced to a definition of the matrix elements on each component  $F$  of the normal vibration.

Below we present the accurate data on the vibration-nuclear transition probabilities in a case of the emission and absorption spectrum of the nucleus of ruthenium  $^{97}\text{Ru}$  ( $E_g^{(0)} = 215$  keV) in the molecule of  $\text{RuO}_4$ . As a molecule has the only normal vibration of the given symmetry type, then the corresponding values of  $b_{ss}$  can be found from the well known Eccart conditions, normalization one and data about the molecule symmetry.

For several normal vibrations of the one symmetry type, a definition of  $b_{ss}$  requires solving the secular equation for molecule  $|GF-IE|=0$  [23-26]. There have been used the results of advanced theoretical calculating electron structure of the molecule within an advanced relativistic scheme of the  $X_{\alpha}$ - scattered waves method (see description in Refs.[23,26]).

In table 1 we present the results of calculating probabilities of the first several the vibration-nuclear transition probabilities in a case of the emission and absorption spectrum of the nucleus of ruthenium  $^{97}\text{Ru}$  ( $E_g^{(0)} = 215$  keV) in the molecule of  $\text{RuO}_4$ .

Table 1  
**The vibration-nuclear transition probabilities in a case of the emission and absorption spectrum of the nucleus of ruthenium  $^{97}\text{Ru}$  in the molecule of  $\text{RuO}_4$ ,**

Vibration transition $v_3^a, v_4^a - v_3^b, v_4^b$	$\bar{P}(v_3^a, v_4^a - v_3^b, v_4^b)$ This work
0,0 - 0,0	0.74
1,0 - 0,0	0.014
0,1 - 0,0	0.067
1,0 - 1,0	0.68
0,1 - 0,1	0.61

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### **Abstract.**

There are firstly presented theoretical data on the vibration-nuclear transition probabilities in a case of the emission and absorption spectrum of the nucleus of ruthenium <sup>97</sup>Ru in the molecule of RuO<sub>4</sub>, estimated on the basis of consistent quantum-mechanical approach to cooperative electron-γ-nuclear spectra (a set of the vibration-rotational satellites in a spectrum of molecule) of multiatomic molecules.

**Key words:** electron-γ-nuclear transition spectrum, multiatomic molecules

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## **О ВЕРОЯТНОСТИ КОЛЕБАТЕЛЬНО-ЯДЕРНЫХ ПЕРЕХОДОВ В СПЕКТРЕ МОЛЕКУЛЫ RuO<sub>4</sub>**

### **Резюме.**

Впервые представлены теоретические данные о вероятностях колебательно-ядерных переходов в случае испускания и поглощения гамма-кванта ядром рутения <sup>97</sup>Ru в молекуле RuO<sub>4</sub>, полученные на основе последовательного квантово-механического подхода к расчету электронно-гамма-ядерного спектра (система колебательно-вращательных спутников в спектре молекуле) в многоатомных молекулах.

**Ключевые слова:** спектр электрон -γ- ядерных переходов, многоатомные молекулы

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## **ПРО ЙМОВІРНІСТІ КОЛІВАЛЬНО-ЯДЕРНИХ ПЕРЕХОДІВ В СПЕКТРІ МОЛЕКУЛИ RuO<sub>4</sub>**

### **Резюме.**

Вперше представлені теоретичні дані про ймовірності колебательно-ядерних переходів у разі випускання і поглинання гамма-кванта ядром рутенію <sup>97</sup>Ru в молекулі RuO<sub>4</sub>, отримані на основі послідовного квантово-механічного підходу до розрахунку електронно гамма-ядерного спектру (система колебательно-обертальних супутників в спектрі молекулі) в багатоатомних молекулах.

**Ключові слова:** спектр електрон -γ- ядерних переходів, багатоатомні молекули