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A. S. Kvasikova

[1]Odessa State Academy of Technical Regulation and Quality, 15, Kovalskaya str., Odessa, 65020, Ukraine
e-mail: quantkva@mail.ru

ON PROBABILITIES OF THE VIBRATION-NUCLEAR TRANSITIONS IN SPECTRUM OF THE RuO_4 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 186Re ($E^{(0)}_{\gamma}$ = 186.7 keV) in the molecule of RuO_4, 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.

From physical viewpint it is obvious that any alteration of the molecular state must be manifested in the quantum transitions, for example, in a spectrum of the γ-radiation of a nucleus (see for example [1-22]). In result of the gamma nuclear transition in a nucleus of a molecule there is arised 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 ^{191}Ir ($E^{(0)}_{g}$ = 82 keV) in the molecule of IrO_4 , ^{188}Os ($E^{(0)}_{g}$ = 155 keV in OsO_4 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 ^{97}Ru in the molecule of RuO_4, 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_4 type; T_d).

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]:

$$H(r_n) = H(r_n^{'}) \exp(-k_{\gamma} u) \qquad (1)$$

where k_g 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:

$$< \Psi_b^* \mid H \mid \Psi_a > \bullet < \Psi_b^* \mid \hat{a}^{-k_{\gamma} u} \mid \Psi_a > \qquad (2)$$

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":

$$M_{ba} \propto \Psi_b^*(r_e) \mid \Psi_a(r_e) > \bullet$$
$$\bullet < \Psi_b^*(R_1, R_2) \mid e^{-k_{\gamma} R_1} \mid \Psi_a(R_1, R_2) > \qquad (3)$$

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:

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

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:

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

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]:

$$\overline{E}_{\text{vib}} = \sum_{v=0}^{\infty} \hbar\omega\left(v + \tfrac{1}{2}\right)\overline{P}(v,0) - \hbar\infty/2 =$$
$$= \sum_{v=0}^{\infty} \hbar\omega\left(v + \tfrac{1}{2}\right)P(v,0) - \hbar\omega/2 =$$
$$= \sum_{v=0} \hbar\omega\left(v + \tfrac{1}{2}\right)\frac{z^v}{v!}e^{-z} - \frac{\hbar\omega}{2} = \frac{1}{2}R\left(\frac{M-m}{m}\right), \qquad (5)$$

where

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

and m is the mass of g-active nucleus, ϑ is an angle between nucleus shift vector and wave vector of g-quantum and line in $\overline{E}_{\text{vib}}$ means averaging on orientations of molecule (or on angles ϑ). To estimate an averaged energy for excitation of the molecule rotation, one must not miss the molecule vibrations as they provide non-zeroth momentum $L = k_v u \sin\vartheta$, 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:

$$\overline{E}_{\text{rot}} = \left\langle \overline{B^2} \right\rangle = B^2 \left\langle u^2 \right\rangle \overline{\sin^2\vartheta} =$$
$$= \tfrac{1}{2} R(B/\hbar\omega)[(M-m)/m] \qquad (6)$$

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:

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

where m is a mass of the g- active nucleus; components of the vector b_{sF} 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:

$$M(b,a) =$$

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

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:

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

for double degenerated vibration in the form:

$$|v_s\rangle = (v_s+1)^{-1/2} \sum_{v_s \sigma_1, v_s \sigma_2, v_s \sigma_3} \Phi_{v_{s\sigma_1}}(Q_{s\sigma_1}) \Phi_{v_{s\sigma_2}}(Q_{s\sigma_2}) \quad (10)$$

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

$$|v_s\rangle = \left(\frac{2}{(v_s+1)(v_s+2)}\right)^{1/2} \times$$

$$\times \sum_{v_s \sigma_1, v_s \sigma_2, v_s \sigma_3} \Phi_{v_{s\sigma 1}}(Q_{s\sigma_1}) \Phi_{v_{s\sigma_2}}(Q_{s\sigma_2}) \Phi_{v_{s\sigma_3}}(Q_{s\sigma_3}) \quad (11)$$

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 $\left| v_s^a \right\rangle$ and $\left| v_s^b \right\rangle$, 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}Ru ($E^{(0)}_g$ = 215 keV) in the molecule of 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 $|GF\text{-}lE|=0$ [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_α- 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}Ru ($E^{(0)}_g$ = 215 keV) in the molecule of RuO_4.

Table 1

The vibration-nuclear transition probabilities in a case of the emission and absorption spectrum of the nucleus of ruthenium ^{97}Ru in the molecule of RuO_4,

Vibration transition $v_3^{\,a}, v_4^{\,a} - v_3^{\,b}, v_4^{\,b}$	$\overline{P}(v_3^{\,a}, v_4^{\,a} - v_3^{\,b}, v_4^{\,b})$ 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 ^{97}Ru in the molecule of RuO_4, 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_4

Резюме.

Впервые представлены теоретические данные о вероятностях колебательно-ядерных переходов в случае испускания и поглощения гамма-кванта ядром рутения ^{97}Ru в молекуле RuO_4, 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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Г. С. Квасикова

ПРО ІМОВІРНОСТІ КОЛИВАЛЬНО-ЯДЕРНИХ ПЕРЕХОДІВ В СПЕКТРІ МОЛЕКУЛИ RuO_4

Резюме.

Вперше представлені теоретичні дані про ймовірності колебательно-ядерних переходів у разі випускання і поглинання гамма-кванта ядром рутенію ^{97}Ru в молекулі RuO_4, 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