NON-RADIATIVE STRUCTURAL POLYMER TRANSITIONS: 'BRIDGING THE QUANTUM GAP' THROUGH NON-RADIATIVE PROCESSES

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ABSTRACT. *Non-radiative structural polymer transitions* are considered in the framework of both *nonlinear solitonic excitations & non-radiative quantum resonance*, which can provide better description of *cascade transport phenomena* of double CC bonds in non-saturated hydrocarbons, *kinetics of photochemical reactions* of the isomer polymer transitions etc – clearly demonstrating that *quantum properties* must be taken into account in these processes.

INTRODUCTION

Various structural transformations of Q1D-molecular chains are characterized by local rearrangements of atoms between neighbor unit cells, with supposed significant role of **low-frequency skeletal vibrations** and their **higher overtones** [1,2]. Namely, neighbor atoms are approaching each other thus increasing probability density for finding charged particles within chemical bonds, which might result in **migrations of conjugated chemical bonds** along Q1D-molecular chain as well as **proton transfer** from a carbon atom to its second neighbor, as it is the case for linear conjugated hydrocarbons [1].

In this context **non-radiative structural polymer transitions** are considered, firstly in the framework of **nonlinear solitonic excitations** which can describe **cascade transport phenomena** of double CC bonds in non-saturated hydrocarbons, and secondly in the framework of **quantum-mechanical non-radiative resonance** which can provide better understanding of **kinetics of photochemical reactions** of the isomer polymer transitions.

NONLINEAR SOLITONIC EXCITATIONS AND NON-RADIATIVE STRUCTURAL POLYMER TRANSITIONS

As excited double CC bond *migrates gradually along conjugated Q1D atomic chain, which passes through corresponding isomeric forms*, this resembles on *solitonic transport of charged particles* (electrons and protons) *along the chain.*

Having this in mind, as well as that interatomic distance is a dominant parameter, the starting point of our theoretical treatment is the *equation for longitudinal oscillations of Q1D atomic chain* [3] *in the field of many-electron energy-configuration hypersurface*:

$$M \frac{d^2 u_n}{dt^2} = k(u_{n+1} - 2u_n + u_{n-1}) + F_{pot} \, ; \tag{1}$$

where *M* is the atomic mass, u_n is the displacement of *n*-th atom from its equilibrium position, while $F_{pot} = - dE_e(x)/dx$ is the restitute force of the chain coupling with the many-electron energy-configuration hypersurface $E_e(x)$.

Also, as *minima of the many-electron energy-configuration hypersurface* correspond to *maxima of probability density of the electronic subsystem* $\left|\Psi_e(r,x,t)\right|^2$, we can formulate this by **variational equation** with the varying Lagrange multiplier (λ):

$$\frac{dE_e(x)}{dx} + \lambda \frac{d\left|\Psi_e(r,x,t)\right|^2}{dx} = 0. \tag{2}$$

Dynamics of Q1D chain, described by Eqs. 1 and 2, implies that classical approach is roughly speaking only 'a part of the picture', so that **quantum properties** of the system *must be taken into account*!

Dynamics of Q1D chain can be *reduced on the well known equation*, by combining Eqs. 1 and 2 with the *development*:

$$u_{n\pm1} = u_n \pm \frac{du_n}{dx} R_0 + \frac{1}{2} \frac{d^2 u_n}{dx^2} R_0^2 + ... \tag{3}$$

which gives:

$$\frac{d^2 u_n}{dt^2} = c^2 \frac{d^2 u_n}{dx^2} + \frac{\lambda}{M} \frac{d\left|\Psi_e(r,x,t)\right|^2}{dx} \tag{4}$$

where $c = R_0 \sqrt{k/M}$ is the *velocity of sound* in the medium, while R_0 is the *interatomic distance*. In the above equation there are two unknown variables, and it is necessary to include into analyisis also **Schrodinger electronic equation**, which has the following form *in the Born-Openheimer adiabatic approximation*:

$$i \frac{\partial \Psi_e (r,x,t)}{\partial t} = (\hat{T}_e + V_{ei} + V_{ee} + V_{ii} + V_{rez}) \Psi_e (r,x,t)$$

(5)

(in $m_e = \hbar = 1$ unit system), with included operators of the *electronic kinetic energy* $(\hat{T}_e)$ and all *Coulomb interactions* of electrons and ions/atomic nuclei (*electron-ion* (V_{ei}), *electron-electron* (V_{ee}), and *ion-ion* (V_{ii})), while the *phenomenologically* introduced term (V_{rez}) represents *resonant interaction* with most probable isomer forms. It is well known that exact solution of the Eq. 5 does not exist, but in a *first approximation* this equation is solved *without electron-electron interaction*, which later appears as a correction in the Hartree-Fock or other approximations [2].

As we are interested in *transport phenomena*, the following assumptions are adopted: *(i) electron(vibron)-phonon interaction is most significant; (ii) electron-electron interaction is neglected; (iii) an excitation arises only on n-th molecular lattice site; (iv) increased excitation probality within the approximation of nearest neighbours* [3].

The *coupling of these excitations and colective oscillations* of the molecular chain can result in *gradual migration of double CC bond along conjugated chain* of unsaturated hydrocarbons [1], which *passes through corresponding isomeric forms* [4], so that local chain deformations reflect themselves on the change of wavefunctions of the electronic subsystem.

Therefore, it is completely legitimate to *"decouple"* in Hamiltonian the *electron-ion* Coulomb interactions regarding *n-th term* and *the others*:

$$V_{ei}\Psi_e(r,x,t) = (-\sum_{\substack{j\alpha \\ \alpha \neq n}} \frac{Ze^2}{r_{j\alpha}} - \sum_{jn} \frac{Ze^2}{r_{jn}})\Psi_e(r,x,t) = (V_{ei}^{j\alpha} + V_{ei}^{jn})\Psi_e(r,x,t).$$

(6)

In accordance with the previous assumption, the *displacement of the n-th molecular lattice site* will change the *electron-ion* Coulomb potential energy of the *electrons localized on this site*, which can be presented by the *development* [5]: $V_{ei}^{jn} \cong V_{ei}^{0} - \chi(u_{n+1} - u_{n-1}) = V_{ei}^{0} - 2\chi R_0 du_n / dx$, where V_{ei}^{0} is a *constant*; besides, the *rest of Coulomb potential energy* ($V_{ei}^{j\alpha}$, V_{ii}, V_{ee}) remains *approximately constant*, which is reasonable if the excitation is localized on only one molecular lattice site [1].

Also, an action of the *operator of the resonant interaction* can be defined, if *most probable isomeric transitions* of unsaturated hydrocarbons with fulfiled $\Delta x = \pm R_0$ are known i.e.:

$$\hat{V}_{rez} \Psi_e(r, x, t) = -J(\Psi_e(r, x + R_0, t) + \Psi_e(r, x - R_0, t)) \qquad (7)$$

where *J* is the *energy of resonant interaction* with equally probable states $\Psi_e(r, x \pm R_0)$, while negative sign appears due to energy balanse.

By combining Eqs. 5 - 7 it follows:

$$i \frac{\partial \Psi_e(r,x,t)}{\partial t} = (\varepsilon_0 + V - 2\chi R_0 \frac{du_n}{dx}) \Psi_e(r,x,t) - J(\Psi_e(r,x+R_0,t) + \Psi_e(r,x-R_0,t)) \quad (8)$$

where $\varepsilon_0 = -\sum_j \Delta_j / 2$ and $V = (V_{ei}^0 + V_{ei}^{j\alpha}) + V_{ii} + V_{ee}$. The obtained Eq. 8 can be further transformed by applying the *continuum approximation*:

$$\Psi_e(r,x \pm R_0,t) = \Psi_e(r,x,t) \pm R_0 \frac{d\Psi_e(r,x,t)}{dx} + \frac{R_0^2}{2} \frac{d^2\Psi_e(r,x,t)}{dx^2} + ... \quad (9)$$

Finally, Eqs. 8, 9 and 4, together with formally *adopted Lagrange multiplier*, $\lambda = 2\chi R_0$, result into well known closed system of **Davydov equtions** [5-7]:

$$i \frac{\partial \Psi_e(r,x,t)}{\partial t} = (\varepsilon_0 + V - 2J - JR_0^2 \frac{d^2}{dx^2} - 2\chi R_0 \frac{du}{dx}) \Psi_e(r,x,t),$$

$$\frac{d^2 u}{dt^2} = c^2 \frac{d^2 u}{dx^2} + \frac{2\chi R_0}{M} \frac{d|\Psi_e(r,x,t)|^2}{dx}, \quad (10)$$

which describe the **soliton nonlinear excitations**.

The properties of the solutions of Eqs. 10 (based on the *classification of nonlinear charged autolocalized excitations in Q1D systems* [8-11], cf. Fig. 1) were explored recently in the case of *non-saturated hydrocarbon polymers*, where it was shown that migration of double CC bond can be described by *adiabatic large polarons – solitons*, with *optical phonons* of the conjugated chains having *major role in skeletal chain deformations* during *soliton-like cascade non-radiative resonant structural transitions via close intermediate participating isomeric forms* [12].

These estimations are also *in accordance* with *theoretical predictions* of the *solitons* in *trans-polyacetilene*, and presence of the *anomalous line in its infrared spectrum* as one of the most convincing evidences for their existence: on the basis of explanation of Scott *et al* the *missing intensity of this infrared line* originates from the *scattering on solitons*, produced by *coupling of intramolecular excitation with in-plane C-H bending vinylene phonon mode*.
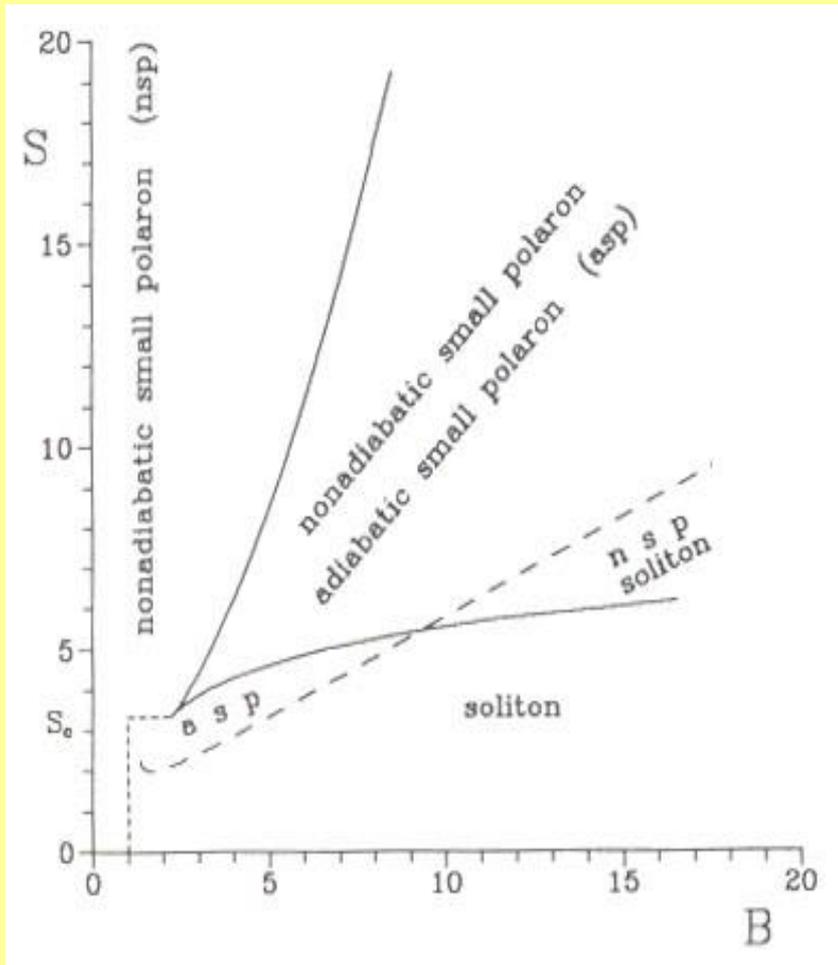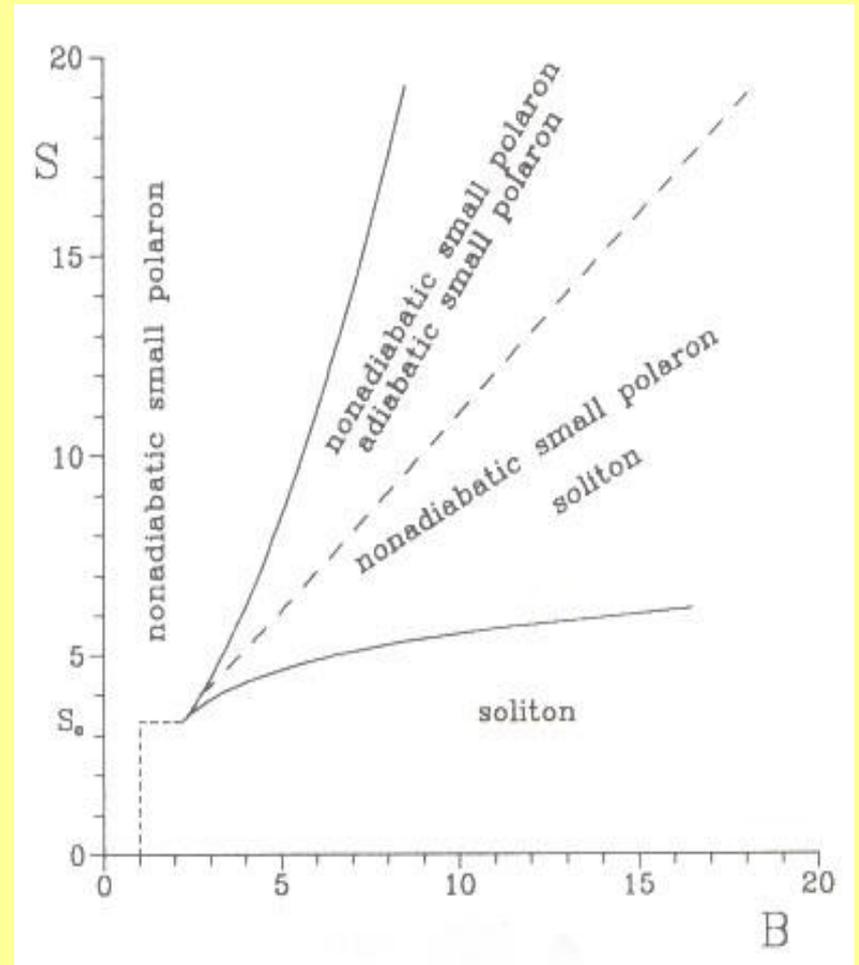
Figure 1. The ***phase diagrams*** of *coupling constant* $(S \sim E_B / \hbar\omega_B)$ *vs. adiabaticity parameter* $(B \sim E_{ex} / \hbar\omega_B)$ in *Q1D exciton-phonon* system, for *exciton coupling* with: (a) *longitudinal acoustic phonons* (ADP-model), and (b) *optical phonons* (MCM-model).

QUANTUM-MECHANICAL RESONANCE AND NON-RADIATIVE STRUCTURAL POLYMER TRANSITIONS

In the framework of the *non-radiative structural polymer transitions* described above, the phenomenon of **quantum-mechanical resonance** (*via* degenerate excited electronic-vibrational states of the close isomer forms) is especially interesting, as it points out *significant role of quantum approach* to description of these transitions. An explanation of this experimentally established phenomenon [13,14] was given by *Gribov* in his monograph [1]. Simply stated, by exciting polymer (thermally, irradiating...) there appears **significant overlap** of the electronic-vibrational wavefunctions of the **two degenerate electronic-vibrational states** (1) and (2) belonging to the **close isomer forms of the polymer**, which gives rise to periodical oscillation back-and-forth between these two close structural polymer states.

In this approach, the **(quasi)classical problem of many-electron energy-configuration hypersurface** $E_e(x)$, *not adiabatically well-defined when traversing between two adjacent local minima* (1) and (2), is **replaced** by better defined problem of the **two (virtually intersecting) isomeric many-electron hypersurfaces (hyperparaboloids)** serving as *potential hypersurfaces for the two vibrational (isomeric) problems* (cf. Fig. 2).
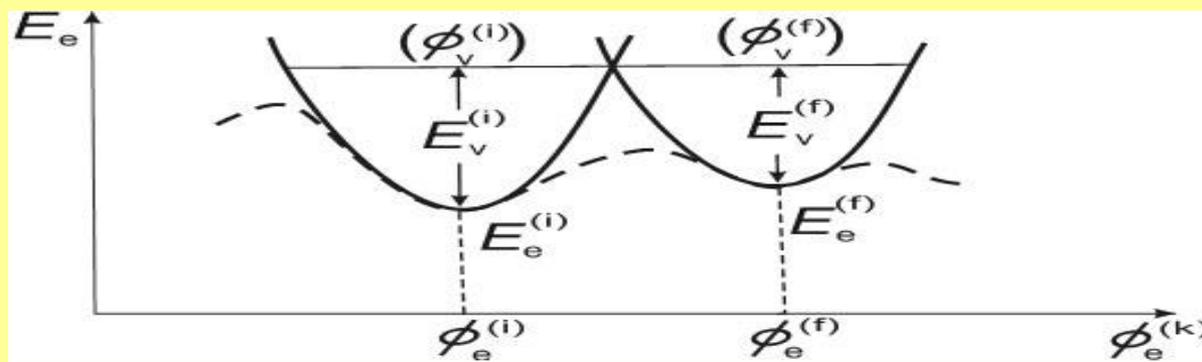
Figure 2. The (quasi)classical problem of **many-electron hypersurface** $E_e(\phi_e^{(k)})$, as a *potential energy* for adiabatically decoupled Q1D *vibrational* and *conformational system* (with local minima as semi-classical 'positions', i.e. many-atomic isomer configurations on many-electron hypersurface (*broken line* in the figure)) - not adiabatically well-defined when traversing between two adjacent local minima - is *replaced* in the **Theory of Non-radiative Resonant Transitions** by better defined problem of **two (virtually intersecting) isomeric many-electron hypersurfaces** (hyperparaboloids) serving as potential hypersurfaces for two *vibrational (isomeric) problems* (*full line* in the figure). In this approach, by **external perturbation** of the isomers, at this very intersection the conditions for **electronic-vibrational non-radiative resonant transitions** between the two isomers (*i, f*) are achieved: in the first approximation, the matrix element of **dipole transition** from *i*-th to *f*-th isomer is given by $\boldsymbol{\mu}^{(i,f)} \approx \boldsymbol{\mu}_e^{(i,f)} S_v^{(i,f)} + \boldsymbol{\mu}_v^{(i,f)} S_e^{(i,f)}$, so that **allowed transitions** between isomeric states (*i, f*) are possible only for **close states** *with nonvanishing* electronic and vibrational dipole moments, $\boldsymbol{\mu}_e^{(i,f)}$ and $\boldsymbol{\mu}_v^{(i,f)}$, *and* electronic and vibrational overlap integrals, $S_v^{(i,f)}$ i $S_e^{(i,f)}$, *or* in **cascade resonant soliton-like transitions** (cf. Fig.2) between *close intermediate participating isomeric states*! Also, during these resonant transitions the perturbed biomolecular system is shortly described by **quantum-coherent superposition** $(\phi_e^{(i)} \phi_v^{(i)} \pm \phi_e^{(f)} \phi_v^{(f)})/\sqrt{2}$, before its **quantum decoherence** into final electronic state $\phi_e^{(f)}$ or into initial electronic state $\phi_e^{(i)}$ (with subsequent deexcitations into lower vibrational states).

Then, by ***external perturbation*** of the isomers, *at this very intersection* the conditions for *electronic-vibrational non-radiative resonant transitions* between the two isomers (1) and (2) *are achieved*: these ***resonance electronic-vibrational states of two isomers*** are transformed from the corresponding (nonperturbed) products of electronic and vibrational stationary wavefunctions $(\phi_e^{(1)}(r,x)\phi_v^{(1)}(x), \phi_e^{(2)}(r,x)\phi_v^{(2)}(x))$ into ***(perturbed) symmetrized stationary superpositions*** $(\phi_e^{(1)}(r,x)\phi_v^{(1)}(x) \pm \phi_e^{(2)}(r,x)\phi_v^{(2)}(x))/\sqrt{2}$, and their (nonperturbed) energies from resonating (equal) superpositions of the ground electronic energies of corresponding minima of many-electron energy-configuration hypersurface and vibrational energies of higher excited states $(E_e^{(1)} + E_v^{(1)} = E_e^{(2)} + E_v^{(2)})$ into ***(perturbed) slightly split energy doublet*** $(E_e^{(1)} + E_v^{(1)} + \frac{1}{2}\Delta E, \ E_e^{(2)} + E_v^{(2)} - \frac{1}{2}\Delta E)$, with $\Delta E = 2(E_e^{(1)} + E_v^{(1)})S_{ev}^{(1,2)}$ (where electronic-vibrational overlap integral between the two resonating isomeric states (1,2) is $S_{ev}^{(1,2)} = \iint \phi_e^{(2)}(r,x)\phi_v^{(2)}(x)\phi_e^{(1)^*}(r,x)\phi_v^{(1)^*}(x)drdx \approx S_v^{(1,2)}S_e^{(1,2)}$, while $S_v^{(1,2)}$ and $S_e^{(1,2)}$ are corresponding ***overlap integrals*** of vibrational and electronic components).

To describe the **temporal aspect of quantum-mechanical resonance** correctly, we start from the *nonstationary electronic-vibrational Schrodinger equation*,

$$i\hbar \frac{\partial \Psi_{ev}(r,x,t)}{\partial t} = (\hat{H}_0 + \Delta H)\Psi_{ev}(r,x,t) \text{,} \tag{11}$$

where ΔH is a nondifferential step-like *perturbation operator*. Then the **solution** of the *nonstationary electronic-vibrational Schrodinger equation* **with perturbation** *is sought in the form* [1]

$$\Psi_{ev}(r,x,t) = a(t)\Psi_{ev}^{(1)}(r,x,t) + b(t)\Psi_{ev}^{(2)}(r,x,t) \text{,} \tag{12}$$

where

$$\Psi_{ev}^{(1)}(r,x,t) = \frac{1}{\sqrt{2}}(\phi_e^{(1)}(r,x)\phi_v^{(1)}(x) + \phi_e^{(2)}(r,x)\phi_v^{(2)}(x))\exp(-i\omega t) \tag{13}$$

$$\Psi_{ev}^{(2)}(r,x,t) = \frac{1}{\sqrt{2}}(\phi_e^{(1)}(r,x)\phi_v^{(1)}(x) - \phi_e^{(2)}(r,x)\phi_v^{(2)}(x))\exp(-i\omega t)(\cos\Delta\omega t - i\sin\Delta\omega t)$$

are the **solutions** of the *nonstationary electronic-vibrational Schrodinger equation* **without perturbation**,

$$i\hbar \frac{\partial \Psi_{ev}(r,x,t)}{\partial t} = \hat{H}_0 \Psi_{ev}(r,x,t) \text{,} \tag{14}$$

with $\omega = (E_e^{(1)} + E_v^{(1)})/\hbar$ ~ 10^{15} Hz and $\Delta\omega = \Delta E/\hbar = 2(E_e^{(1)} + E_v^{(1)})S_{ev}^{(1,2)}/\hbar$ ~ 10^9 Hz [1], while $a(t)$ and $b(t)$ are time-dependent functions, which can be determined by insertion of Eq. 12 into Eq. 11 (knowing that wavefunctions of Eqs. 13 are solutions of Eq. 14), so that we get *two differential equations*, $i\hbar\partial a/\partial t = a\Delta H$ and $i\hbar\partial b/\partial t = b\Delta H$, with *solutions* $a(t) = b(t) = \exp(-i\Delta H t/\hbar)$ (fulfiled for the initial condition $\left|\Psi_{ev}(r,x,0)\right|^2 = \left|\phi_e^{(1)}(r,x)\phi_v^{(1)}(x)\right|^2$, when $a(0) = b(0) = 1/\sqrt{2}$).

By inserting Eqs. 13 and solutions for $a(t)$, $b(t)$ into Eq. 12, with some algebriac manipulation, the *time-dependent probability density* of the *electronic-vibrational wavefunction* of the system is obtained:

$$\left|\Psi_{ev}(r,x,t)\right|^2 = \frac{1}{2}\left|\phi_e^{(1)}(r,x)\right|^2\left|\phi_v^{(1)}(x)\right|^2\cos^2\frac{\Delta\omega}{2}t + \frac{1}{2}\left|\phi_e^{(2)}(r,x)\right|^2\left|\phi_v^{(2)}(x)\right|^2\sin^2\frac{\Delta\omega}{2}t \quad (15)$$

On the basis of Eq. 15, it can be concluded that *system alternatively excites two isomer-conformational states with periodicity T = 1/Δω ~ 10⁻⁹*

On the basis of Eq. 15, it can be concluded that *system alternatively excites two isomer-conformational states with periodicity T = 1/Δω ~* 10^{-9} s, which is *macroscopically manifested* as a *temporal change in concentration of the two isomers* in the two-isomer polymer solution.

Thus obtained probability of finding temporal evolution of the resonating doublet state of such a system, served to *Gribov and colleagues* [15,16] as a basis to explore the **kinetics equations** *for populated polymer electronic-vibrational levels in photochemical reactions of isomer transitions*.

In particular, we shall here consider the **model photochemical reaction** *of isomer transitions* **for two-isomeric polymer system with four energy levels**, where the system is **initially excited** by some *external optical perturbation* ΔH , *from the first-isomer ground energy state* (3) *into its excited energy state* (1). This causes an **intense overlap** of the *wavefunctions of the* **two excited isomer forms** (1) and (2), which exibit **resonant fluctuating** *back-and-forth* **chemical-isomer transitions** $(1) \leftrightarrow (2)$ (defined by corresponding *time-dependent probabilities* $w_{12} = w\cos^2 \Delta\omega t$ and $w_{21} = w\sin^2 \Delta\omega t$, cf. Eq. 15), *also accompanied by* **spontaneous isomer deexcitations** $(1) \to (3)$ and $(2) \to (4)$ into *corresponding isomer ground states* (defined by *time-independent probabilities* w_{13} and w_{24}, respectively). Accordingly, we easily obtain the corrsponding **system of kinetics equations**:

$$\frac{dn_1}{dt} = -w_{13}n_1 - wn_1 \cos^2 \Delta\omega t + wn_2 \sin^2 \Delta\omega t \; ;$$

$$\frac{dn_2}{dt} = -w_{24}n_2 + wn_1 \cos^2 \Delta\omega t - wn_2 \sin^2 \Delta\omega t \; ;$$

$$\frac{dn_3}{dt} = w_{13}n_1 \; ;$$

$$\frac{dn_4}{dt} = w_{24}n_2 \; .$$

(16)

with ***concentrations*** n_j (*j* = 1, ..., 4) of polymers occupying these four electronic-vibrational levels. By *solving numerically* the above system of equations (with *model-adopted probabilities* $w = 0.7$, $w_{13} = 0.1$, $w_{24} = 0.2$, *resonant frequency of fluctuating back-and-forth chemical-isomer transitions* $\Delta\omega = 10^9$ Hz, time scale in 10^{-9} s, and *polymer isomer concentrations n_j in relative units*), ***graphical temporal dependance*** of the four relative polymer concentrations is obtained, cf. Fig. 3.
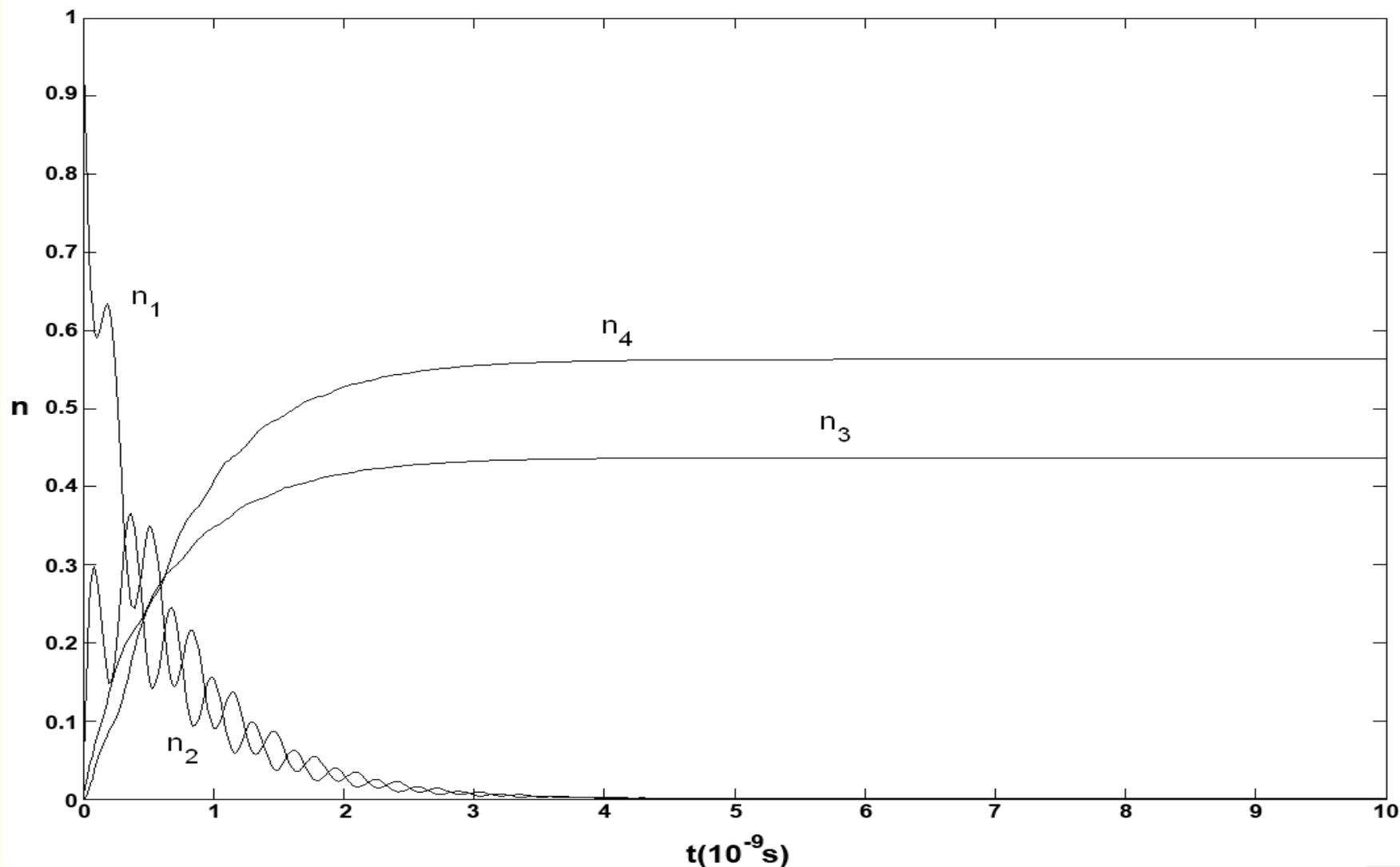
Figure 3. The *kinetics of polymer concentrations n_j* (in relative units) in the model *photochemical reaction of isomer transitions*, for two-isomeric polymer system with each isomer in possible ground and excited electronic-vibrational states.

By analysis of this graph, it is obvious that *effect of quantum-mechanical resonance* between the first-isomer excited state (1) and the second-isomer excited state (2), **increases the population** n_4 of the second-isomer ground state (4) as a consequence of *external spontaneous deexcitation* of the second-isomer excited state (2). We should also address the following question: *what is the reason for **different concentrations** of the populated ground electronic-vibrational levels* (3) and (4), resulted by spontaneous deexcitations of the corrersponding excited resonant levels (1) and (2) of the two isomer forms (as these *two excited forms* (1) and (2) are *equally probable* due to quantum-mechanical resonance)?

The answer is that the *stable isomer forms* of the polymer are related to **different "depths" of potential wells** or energies of the polymer *ground electronic-vibrational levels* ($E_{ev}^{(3)} \neq E_{ev}^{(4)}$), causing by thermodynamical equilibration with environment that *concentrations of deexcited ground states* (3) and (4) of the two isomers *are different* (according to: $n_j = \beta \exp(-E_{ev}^{(j)}{}_{ev} / kT)$, where *j* = 3, 4 and $0 < \beta < 1$).

CONCLUSION

In this paper *non-radiative structural polymer transitions* are considered, firstly in the framework of *nonlinear solitonic excitations* which can describe *cascade transport phenomena of double CC bonds in non-saturated hydrocarbons*, and secondly in the framework of *quantum-mechanical non-radiative resonance* which can provide better understanding of *kinetics of photochemical reactions of the isomer polymer transitions.*

This clearly demonstrates that *quantum properties must be taken into account in these processes* for their deeper understanding.

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