Physical Chemistry

On the problem of directed signal transmission and energy transfer in molecular systems

L. A. Gribov

V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences,
19 ul. Kosygina, 119991 Moscow, Russian Federation.
Fax: +7 (095) 938 2054. E-mail: gribov@geokhi.ru

A new physical interpretation of the mechanism of directed energy transfer and signal transmission in molecular systems along one-dimensional chains capable of successive isomerization is proposed. The photoacceptor—transmitting chain—reaction center system is considered as a model. Conditions under which the directed energy transfer occurs from the photoacceptor to the reaction center along the chain are analyzed. The time of signal transmission depends on the chain length, and the transmission coefficient is mainly determined by the characteristics of the initial and final elements in the whole system.

Key words: successive isomerization, signal transmission, molecular converter.

The problem of directed energy transfer and signal transmission at long (in the molecular scale) distances in nanosystems has been discussed for long. Photosynthesis is a typical example of the process in which such a transfer (transmission) plays the determining role. In this case, the absorption of energy in the form of a photon occurs within one part of a supramolecular system containing large planar molecular aggregates with well-developed conjugated structure, while the reaction itself, whose products are the final stage of the overall process, proceeds in the different spatial region at a long (in the molecular scale) distance from the photoabsorbing center (photoacceptor).

The real process of photosynthesis is very complicated, occurs in several stages, and has not been completely studied so far. The purpose of this work is an attempt to explain for the model how the light energy supplied from an external source and was initially localized within the photoacceptor, is then transferred along the one-dimensional and seemingly non-conducting chain to the reaction center.

Only few possibilities of spatial transfer of energy and signal transmission are known in physics. Signal transmission in the form of electromagnetic field (re-absorption of light and diffusion of radiation) is obviously insignificant in the molecular world. There are no conventional conductors in this case. No excitons are formed in one-dimensional chains. Ionic currents can flow in the medium, but they seem to be inefficient for the directed transmission of signals. Induction-resonance (dipole-dipole) and exchange-resonance interactions are barely efficient. The characteristic fact of linking energy-acceptor

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 213—219, February, 2002.

groups and distant reaction centers by one-dimensional molecular chains suggests that precisely these chains can be channels of energy transfer and signal transmission.

Remind that the mechanism of energy transfer in the photosynthetic process is interpreted, in general, as follows: a photon, being absorbed, excites an electron and transits it to almost free state, and then it migrates along the molecular chain to the reaction center where the reaction occurs (see, *e.g.*, Ref. 1).

This commonly accepted view on the mechanism of energy transfer from the absorption site *via* the transfer of an electron, which then participates in the final stage of the reaction, provokes at least two principal objections.

The first objection is that no significant changes, from the viewpoint of the structure and properties of the electronic shell, can occur in the photoacceptor group upon absorption of a photon with the energy close to that of the longest-wave electron-vibrational transition in this group, if it is really a large molecular structure with the developed conjugation. Moreover, no "ultra"-mobile electron cannot form. This assertion is based on the results of numerous calculations (see Ref. 2 and references cited therein) of the vibrational structure of electronic spectra of large systems with developed conjugation. Almost all of them are performed assuming minor changes in the potential surfaces (PS) of the electron-excited states (EES) compared to the PS of the ground state. This is obvious because in large systems with a great number of electrons a change in the MO of one of them cannot introduce substantial perturbations to the properties of the whole electron shell. Then it is quite unclear how the "mobile" electron can migrate along the molecular chain which usually contains fragments with non-conjugated bonds? The principle of short-range action is a fundamental one in physics. Therefore, along the whole pathway the electron should be effected by the quasi-static electric field, which is directed. From where this field appears? It should also be taken into account that the energy levels of not very long chains do not form energy bands even at very developed conjugation, which is necessary but insufficient for almost free motion of an electron along the chain.

We considered the transfer of photoexcitation. However, it is known that the energy of a chemical reaction, which occurs at one end of the chain, can be transmitted through the connecting molecular chain at rather long distances to stimulate another reaction at the distant end of the chain.

Therefore, the problem of energy transfer and signal transmission (in broad sense) along organic one-dimensional chains is much more general.

In this work, we propose a specific interpretation of this phenomenon, based on the concept of concerted, consecutive isomer—isomer (II) transformations in the chain. Generally speaking, this point of view is not quite new. Migrations of multiple bonds along one-dimensional chains or side groups attached to the chains (for example, transfer of the BH_2 group in alkylboranes) are well known. In essence, these processes represent signal transmission and energy transfer because a multiple bond with a greater strength than that of a single bond can be associated with a region of high energy and electron density against the background of less energetically capacious chain regions.

Therefore, the problem is to explain the mechanism of directivity of this process and to reveal necessary conditions for the molecular effect of signal transmission (non-uniformity).

Let us consider this problem taking a simple model system comprising the light absorbing center (photoacceptor), the transmitting molecular chain capable of undergoing isomerization, and the reaction center as an example. For clarity, we will choose the $A—CH=CH_2—(CH_2)_n—R$ system, where A is the photoaccepting group and R = COOH is the carboxyl group, as the model.

Due to the successive migration of the C=C double bond the system can undergo isomerization into the form $A—(CH_2)_n—CH=CH—R$. Hereafter, the chain fragment between the photoacceptor A and the group R will be designated as B.

In treating the problem we will be guided by the available concepts[3—8] of isomerization and bimolecular reactions.

Assume that the system absorbs a photon with an energy corresponding to the longest-wavelength band in the electronic spectrum. Evidently, this corresponds to the transition of an electron from the highest occupied MO to the lowest unoccupied MO of the photoaccepting group A (π—π-transition). Since any MO to some extent fills the whole molecular space, we can say that light absorption causes a transition of the ABR system to the first EES. It will be recalled that the 0—0 optical transition, for which no normal vibrations are excited, is the most probable. However, for further considerations we have to take into account that zero-point vibrations always exist.

Now let us assume that the ABR system in the ground state can undergo a relatively easy isomerization and can take the forms $(ABR)^{(1)}$, $(ABR)^{(2)}$, $(ABR)^{(3)}$, *etc.* In the model chosen, this corresponds to transfer (migration) of the C=C bond along the chain. Since, as mentioned above, in large systems the PS of weakly excited electronic states differ only slightly from the ground-state PS, we can postulate the existence of analogous sequences of the isomeric structures $(ABR)^{*(1)}$, $(ABR)^{*(2)}$, *etc.* for the lowest EES.

Previously,[3,8] we have shown that the states corresponding to all isomeric forms of a molecular system, including the states corresponding to the first stage of decomposition (the so-called "pre-reaction isomerization"), at which transfer of atoms due to large-amplitude vibrations results in such electron density redistributions that some chemical bonds weaken substantially and other bonds are formed, can be mathematically described by a common energy matrix ***H***. The role of "linking" quantities is played by the off-diagonal matrix elements, which in the Franck—Condon approximation have the form

$$h^{(k,n)} = 1/2(E_{\text{ev}}{}^{(k)} + E_{\text{ev}}{}^{(n)})S_{\text{e}}{}^{(k,n)}S_{\text{v}}{}^{(k,n)},$$

where $E_{\text{ev}}{}^{(k)}$ and $E_{\text{ev}}{}^{(n)}$ are the electron-vibrational energies of the kth and nth isomers, respectively, and $S_{\text{e}}{}^{(k,n)}$ and $S_{\text{v}}{}^{(k,n)}$ are the overlap integrals of the electronic and vibrational cofactors of the full adiabatic electron-vibrational functions of the interacting isomeric structures. For the state of "pre-decomposition isomerization," the $E_{\text{ev}}{}^{(k)}$ energy includes the temperature-dependent energy of translational motions of the decomposition products while the vibrational eigenfunction $\psi_{\text{v}}{}^{(k)}$ has the form $\psi_{\text{v}}{}^{(k)} = \psi_{\text{v}'}{}^{(k)}\psi_{\text{tr}}{}^{(k)}$, where $\psi_{\text{v}'}{}^{(k)}$ is the eigenfunction corresponding to internal vibrations of the reaction products and $\psi_{\text{tr}}{}^{(k)}$ is the function describing the relative motion of the reaction products.

Assuming independence of the systems of energy levels for different isomeric forms, we can meet pairs of the energy levels with equal energies (random degeneracy). In solving the problem using the ***H*** matrix taking into account the interactions between the isomeric forms, this will result in resonance and the appearance of "diffuse" states with the functions

$$\psi^{(k,n)} = \frac{1}{\sqrt{2}}(\psi_{\text{cv}}^{(k)} \pm \psi_{\text{cv}}^{(n)}).$$

Degeneration is removed, and a resonance doublet appears.

Imposition of the nearly arbitrary time-dependent perturbation on such a combined system assuming that initially it was in the state $\psi_{\text{ev}}{}^{(k)}$ leads to the appearance of quantum beats (periodical transitions from the state with the $\psi_{\text{ev}}{}^{(k)}$ function to the state with the $\psi_{\text{ev}}{}^{(n)}$ function). These transitions, which occur without changing the energy (along the degenerate level), are the II transitions. It is reasonable to relate their probability to the beat frequency and the $h^{(k,n)}$ matrix element. The larger the latter, the higher the probability of the II transition. The direct ($k \to n$) and inverse ($n \to k$) transitions occur equiprobably.

It is of interest that quantum beats arise only in the case of pair resonance and not for triple or higher resonances. This means that transitions are possible only between pairs of isomers with slightly different structures.[8]

Now let us consider the main problem, *viz.*, signal transmission along the chain.

Previously,[5—8] it has been shown that migration of the double bond or transfer of the side group can occur due to both large-amplitude vibrations (high overtones) of the chain skeleton atoms and protons transfer due to these vibrations. In the model discussed, the C=C bond migrates due to the counter motions of the proton of the "left" C—H bond in the —HC=CH—CH_2— fragment and two protons of the "right" CH_2 group, induced by the highly excited overtone "kink" vibration of the C=C—C angle of the molecular skeleton (see Ref. 6). The isomerization effect is always local because the structure of the combining isomers cannot change significantly.

Large-amplitude vibrations in the chain can be excited only when the zero vibrational level of the first EES of the initial isomer, $(\text{ABR})^{*(1)}$, resonates with the high vibrational level of the EES of another isomer and the $h^{(k,n)}$ matrix element is sufficiently large to provide fast isomerization.

For resonance of the zero vibrational level of the EES of the first isomer with one of the higher vibrational levels of the electron-excited combining state to occur, it is necessary that the corresponding potential well of the second isomer be deeper than the well of the first isomer by the appropriate vibrational quantum.

Remind that the II transitions are always electron-vibrational and non-adiabatic, although the corresponding eigenfunctions are constructed from adiabatic components.

Note that if the EES is triplet and appeared due to the collision loss of energy by the initial singlet state, a vibrational motion described by nonzero vibrational quantum numbers can be excited in the initial isomer.

This also can happen if not the lowest EES but the state next in energy was excited first.

To transfer the energy supplied to the chain due to absorption of a photon to provide successive isomerization (migration of the double bond), one needs that the vibrations of the group A be not local for this group but also coupled with the vibrations of the adjacent chain fragments. In addition, the vibrational wavefunction of at least one of these vibrations even at zero vibrational quantum numbers should be "diffuse" to sufficiently high extent to provide substantial overlapping (the overlap integral) with the vibrational wavefunction of the resonant state of the second isomer. This is possible if the vibrations are non-characteristic of group A and (simultaneously) low-frequency. In this case, the corresponding cross section of the potential well of the first isomer is broad and can partially cover the region of the potential well of the second isomer. It should also be taken into account that the II transformation is always local and related, as a rule, to the rearrangement of adjacent atoms. If all these conditions are fulfilled, the corresponding II transition occurs. Local isomerizations are well known and consistent with the theory proposed earlier.[5—8]

In this work we calculated the vibrational spectrum of a model system consisting of a naphthalene molecule to which a rather long —CH=CH—$(CH_2)_n$—R chain is attached and showed that the naphthalene molecule executes low-frequency vibrations involving both the molecule itself (group A) and the hydrocarbon chain. This implies that if the transitions between the MO upon photoexcitation are local and cause a change in the electron density distribution only within the naphthalene fragment, many of the low-frequency vibrations are nonlocal. This first of all concerns the nonplanar vibrations of the naphthalene molecule, which are easily coupled with the deformation vibrations of the chain, especially when the symmetry plane of the chain is perpendicular to the ring plane. In this case, the motions of the C atom shared by the chain and the naphthalene fragment are collinear for both chain vibrations and angular vibrations of the skeleton. This leads to a resonance of vibrations and to its propagation over the whole molecule. The resulting strongly coupled nonlocal vibrations with frequencies $\nu \approx 100$, 260, and 290 cm^{-1} are characterized by a strong decrease in the C(1)=C(2)—C(3) angle, especially for the vibration with a frequency of 290 cm^{-1}. The vibration amplitudes of the angle are equal to 0.32, 0.79, and 0.84 relative units, respectively. It is this deformation of the C(1)=C(2)—C(3) angle that can promote[6] the counter "jump" of protons and migration of the double bond. In this case, the angular vibration of the C(2)—C(3)=C(4) fragment of the second isomer is high-energy if the potential well of the second isomer is deeper than that of the first isomer (Fig. 1) and if the nonradiative transition along the degenerate level occurs to one of the higher vibrational levels. This provides the possibility of further migration of the double bond due to the angular vibration of the C(2)—C(3)=C(4) fragment.

The aforesaid allows us to formulate the first necessary condition for signal transmission and energy transfer along the chain. Such a transmission (transfer) is possible if the set of isomeric structures of the ABR system includes a structure for which the energy difference $E_e(ABR)^{*(1)} - E_e(ABR)^{*(2)}$ is sufficient to excite large-amplitude vibrations (highly excited overtones) in the second isomer (in the chain) at resonance of the electron-vibrational energy levels of the second isomer and the initial structure and provided a rather large value of the $h^{(1,2)}$ matrix element determined by the product of the $S_e^{(1,2)}$ и $S_v^{(1,2)}$ overlap integrals.

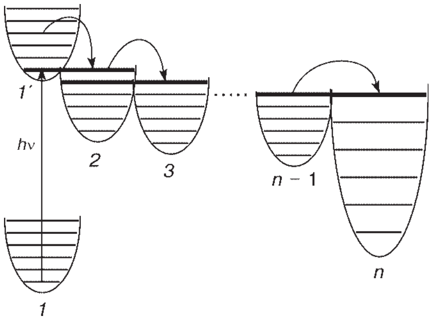

Fig. 1. Scheme of the sequence of potential wells corresponding to the isomeric structures (1, 2, ..., *n* – 1). The well labeled with *n* corresponds to decomposition. The lowest well at the left (*1*) corresponds to the ground state of the initial structure. The other wells (*1´*, *2*, *3*, ..., *n* – 1) correspond to the electronic-excited states. The resonant levels are marked by bold lines. The sequence of isomeric transformations is *1´ → 2*, *2 → 3*, *etc*.

If the $(ABR)^{*(1)}$ state was populated first, the second structure is populated *via* the nonradiative transition (either isomer—isomer or a transition resulting in the decomposition of the R group, see below). The population kinetics can be described as follows. Let the II transformation be a result of the quantum beats appeared upon perturbation of the stationary resonance doublet states of the isomeric structures. The probability of the II transformation (β) is determined by the beat frequency and the direct and inverse transitions occur equiprobably. Then these reactions should be treated as reversible. The real yield of the product (accumulation of the second isomer) is determined not only by the β value but also by the population differences between the resonant levels of the isomeric structures. At constant temperature, the Boltzmann population of the energy levels of the isomers is also constant. The following important circumstance should be kept in mind: positions of the resonant levels on the energy scale are determined by the sum of the electronic and vibrational energies; therefore, equality of the total electron-vibrational energies does not imply equality of their vibrational components.

For a steady-state process at constant temperature, the population of the energy level of a particular isomer is determined only by the vibrational component of the total energy. If the electronic energies of the isomers differ, at resonance the corresponding vibrational energies, which are always measured from the energy of zero-point vibrations of the isomer, are also different. As a result, the populations of the vibrational levels of the isomers at the same temperature can be differeent.

For two isomers, the derivatives dn_1/dt and dn_2/dt (n_1 and n_2 are the numbers of molecules of the first and second isomers per unit volume, respectively, and t is time) can be written as

$$dn_1/dt = -\beta n_1 \exp(-E_v^{(1)}/kT) + \beta n_2 \exp(-E_v^{(2)}/kT),$$

$$dn_2/dt = \beta n_1 \exp(-E_v^{(1)}/kT) - \beta n_2 \exp(-E_v^{(2)}/kT),$$

or

$$dn_1/dt = -\beta^{(1,2)} n_1 + \beta^{(2,1)} n_2,$$

$$dn_2/dt = \beta^{(1,2)} n_1 - \beta^{(2,1)} n_2,$$

where $\beta^{(1,2)} = \beta\exp(-E_v^{(1)}/kT)$, $\beta^{(2,1)} = \beta\exp(-E_v^{(2)}/kT)$, and k is the Boltzmann constant.

At $E_v^{(1)} = E_v^{(2)}$ and established equilibrium, $\mathrm{d}n_1/\mathrm{d}t = \mathrm{d}n_2/\mathrm{d}t = 0$; taking into account the equality $\beta^{(1,2)} = \beta^{(2,1)}$, we get $n_1 = n_2$, *i.e.*, both isomers are present in equal amounts after completion of the reaction.

If the well corresponding to the first isomer is more shallow than that of the second isomer (*i.e.*, $E_v^{(1)} < E_v^{(2)}$ and $\beta^{(1,2)} > \beta^{(2,1)}$), then $n_1 < n_2$ and the second isomer is mostly accumulated. Otherwise, if $E_v^{(1)} > E_v^{(2)}$, predominant concentration of the first isomer is retained.

Initially (at $t = 0$), one gets $-\mathrm{d}n_1/\mathrm{d}t = \mathrm{d}n_2/\mathrm{d}t = \beta^{(1,2)}n_1(0)$, where $n_1(0)$ is the initial number of the molecules of the first isomer per unit volume. The net result of the reaction depends on the ratio of the well depths: the deeper the potential well (or the lower the electronic energy of a particular isomeric structure), the higher the concentration of this structure. In any case, the initial rate of the process depends on the reaction probability (beat frequency) and on the population of the "resonant" energy level of the initial isomer.

In the matrix form, the general solution for $n_1(t)$ and $n_2(t)$ can be written as follows:

$$\begin{bmatrix} n_1 \\ n_2 \end{bmatrix} = \begin{bmatrix} n_1(0) \\ 0 \end{bmatrix} + At\begin{bmatrix} n_1(0) \\ 0 \end{bmatrix} + \frac{t^2}{2!}A^2\begin{bmatrix} n_1(0) \\ 0 \end{bmatrix} + \ldots = \exp(At)\begin{bmatrix} n_1(0) \\ 0 \end{bmatrix}$$

where the matrix A has the form $A = \begin{bmatrix} -\beta^{(1,2)} & \beta^{(2,1)} \\ \beta^{(1,2)} & -\beta^{(2,1)} \end{bmatrix}$.

Figures 2 and 3 present some time plots of the populations of the isomeric structures, constructed assuming that the first potential well is more shallow than the second well. This manifests itself as different temperature populations and probabilities of transitions from the first to the second well and *vice versa* (see the matrix A). As can be seen, some time after the beginning of the reaction the system reaches an equilibrium, which depends on the initial conditions. If they are changed, the equilibrium is shifted, which is characteristic of reversible processes.

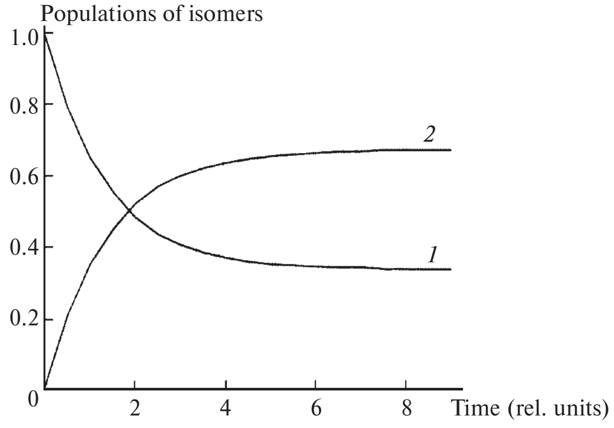

Fig. 2. Populations of the first (curve *1*) and second (curve *2*) isomers plotted as functions of time. The first isomer is populated first.

Matrix A: $A = \begin{bmatrix} -0.5 & 0.25 \\ 0.5 & -0.25 \end{bmatrix}$, initial conditions: $x\big|_{t=0} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$.

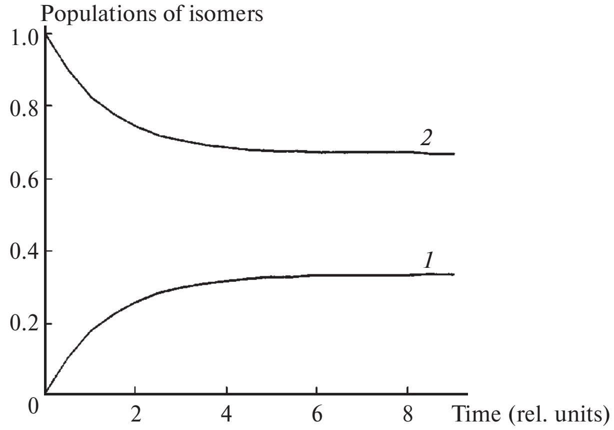

Fig. 3. Populations of the first (curve *1*) and second (curve *2*) isomers plotted as functions of time. The second isomer is populated first.

Matrix A: $A = \begin{bmatrix} -0.5 & 0.25 \\ 0.5 & -0.25 \end{bmatrix}$, initial conditions: $x\big|_{t=0} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$.

Now let us consider the results of changes in the populations for the chains of II transformations (four and ten isomeric structures) using the mathematical models. In Fig. 4, the well depth uniformly increases on going from the first to third potential well, which results in the uniform change in the probabilities of the direct and inverse transitions: $\beta^{(1,2)} = 0.9 > \beta^{(2,1)} = 0.8 > \beta^{(2,3)} = 0.7 > \beta^{(3,2)} = 0.6 > \beta^{(3,4)} = 0.5 > \beta^{(4,3)} = 0.3$. On going to the fourth well, a stepwise change in the well depth occurs and the population of this well in the final stage of the process is $n_4 \approx 0.4$ ($n_1 \approx 0.2$). Changes in the populations of the isomeric structures with time are determined by the initial conditions and for the case of four isomers are described by the system of four kinetic equations

$$\mathrm{d}n_1/\mathrm{d}t = -n_1\beta^{(1,2)} + n_2\beta^{(2,1)},$$

$$\mathrm{d}n_2/\mathrm{d}t = n_1\beta^{(1,2)} - n_2[\beta^{(2,1)} + \beta^{(2,3)}] + n_3\beta^{(3,2)},$$

$$\mathrm{d}n_3/\mathrm{d}t = n_2\beta^{(2,3)} - n_3[\beta^{(3,2)} + \beta^{(3,4)}] + n_4\beta^{(4,3)},$$

$$\mathrm{d}n_4/\mathrm{d}t = n_3\beta^{(3,4)} - n_4\beta^{(4,3)}.$$

For ten isomers, the system of equations is constructed similarly.

As previously, we will consider that $\beta^{(2,1)} \neq \beta^{(1,2)}$ *etc.* due to the temperature dependence of the population of the energy levels and that the transitions from the preceding to the given structure and from the given to succeeding structure occur as a result of resonances of different pairs of energy levels (solid lines in Fig. 1). The population n_j is a characteristic of the whole isomeric state rather than particular level.

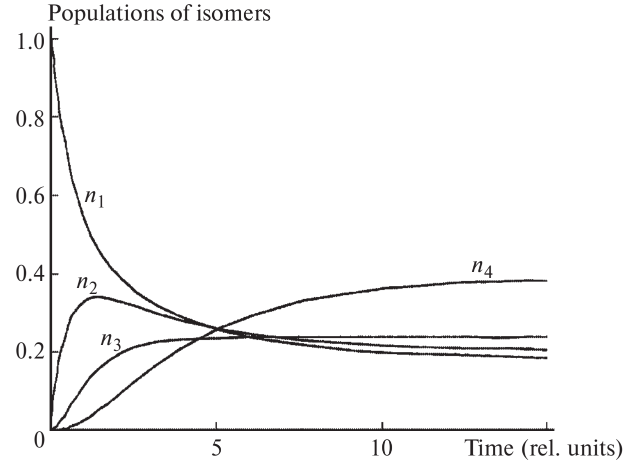

Fig. 4. Populations n_i plotted as functions of time for the system of four isomeric structures. Initial conditions: $n_1 = 1$, $n_2 = n_3 = n_4 = 0$. The depths of wells are nearly equal.

The results of our model calculations are presented in Figs. 4—9. As can be seen, nearly complete disappearance of the initial isomer and complete population of the last isomer (this can also be the state corresponding to the first stage of a bimolecular reaction, see above) requires that the last potential well be much deeper than the first well. The process follows the path corresponding to a decrease in the energy of the final structure. Evidently, the deepest potential well corresponding to the final state of the system is reached in the case of a bimolecular decomposition reaction because carrying out the reaction requires much higher energy than isomerization. Therefore, energy transfer completed with decomposition should be considered the most favorable. This is accompanied by considerable expenditure of energy for the separation of the decomposition products from the chain.

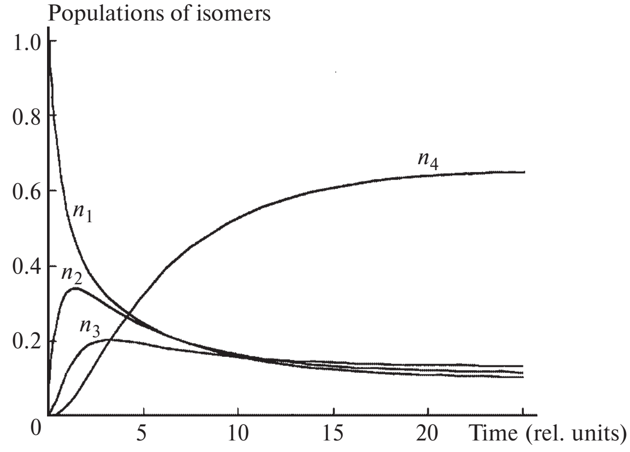

Fig. 5. Populations n_i plotted as functions of time for the system of four isomeric structures. For the initial conditions, see Fig. 4, but the fourth well is deeper ($\beta^{(4,3)} = 0.1$); after completion of the process $n_4 = 0.65$ ($n_1 \approx 0.1$).

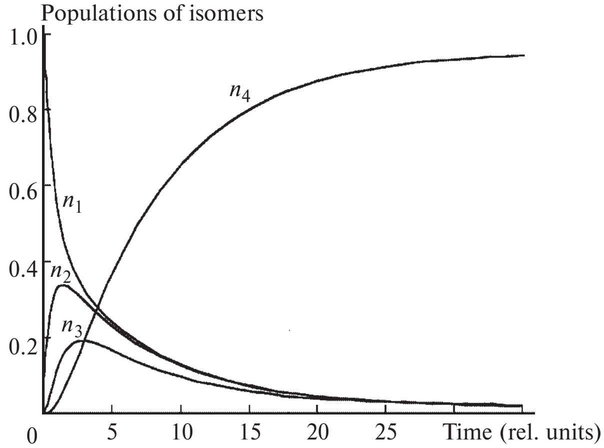

Fig. 6. Populations n_i plotted as functions of time for the system of four isomeric structures. For the initial conditions, see Fig. 4. The fourth well deepens ($\beta^{(4,3)} = 0.01$); after completion of the process $n_4 = 0.95$ and $n_1 \approx 0.1$.

It is of paramount importance that the net result is independent of the chain length: in any case, the population is completely transferred to the distant end of the chain. The duration of the process depends on both the chain length and the probabilities of transitions between neighboring wells (in particular, on the well depths ratio).

The highest efficiency of the conducting system is achieved when the sequence of isomers is such that the well of each succeeding isomer is slightly deeper than that of the preceding isomer. Then the population of the initial isomer is nearly completely transferred to the final structure. However, this is not to say that the process is impossible when this condition is not fulfilled. Figures 7

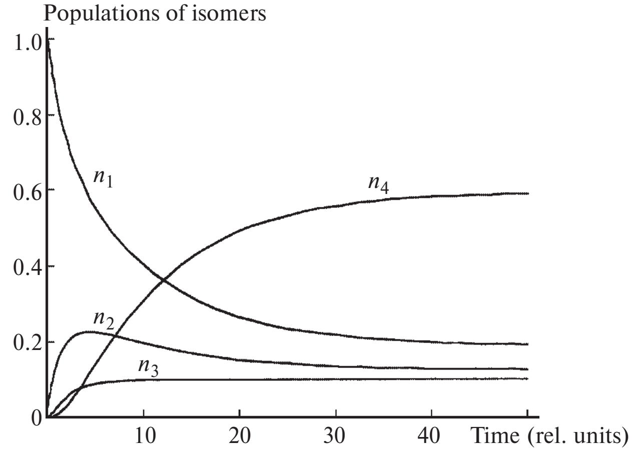

Fig. 7. Populations n_i plotted as functions of time for the system of four isomeric structures. For the initial conditions, see Fig. 4. The well depth decreases on going from the first to the third potential well. Transition probabilities: $\beta^{(1,2)} = 0.2$, $\beta^{(2,1)} = 0.3$, $\beta^{(2,3)} = 0.4$, $\beta^{(3,2)} = 0.5$, $\beta^{(3,4)} = 0.6$, $\beta^{(4,3)} = 0.1$. High final population of the fourth well is observed ($n_4 \approx 0.6$). The population of the first well remains unchanged ($n_1 = 0.2$).

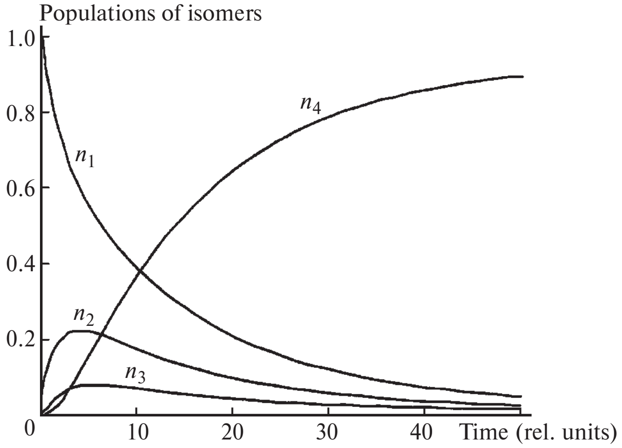

Fig. 8. Populations n_i plotted as functions of time for the system of four isomeric structures. For the initial conditions, see Fig. 7. The fourth well deepens ($\beta^{(4,3)} = 0.01$); after completion of the process $n_4 = 0.9$ and $n_1 \approx 0.05$.

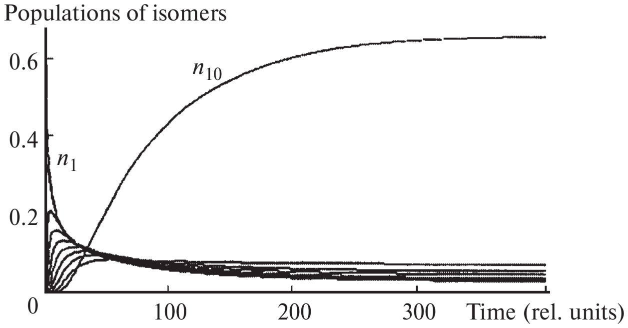

Fig. 9. Results of the solution of the model problem for the system with ten potential wells with uniformly increasing depths ($\beta^{(1,2)} = 0.9$, $\beta^{(2,1)} = 0.85$, $\beta^{(2,3)} = 0.80$, $\beta^{(3,2)} = 0.75$, $\beta^{(3,4)} = 0.70$, $\beta^{(4,3)} = 0.65$, $\beta^{(4,5)} = 0.60$, $\beta^{(5,4)} = 0.55$, $\beta^{(5,6)} = 0.50$, $\beta^{(6,5)} = 0.45$, $\beta^{(6,7)} = 0.40$, $\beta^{(7,6)} = 0.35$, $\beta^{(7,8)} = 0.30$, $\beta^{(8,7)} = 0.25$, $\beta^{(8,9)} = 0.20$, $\beta^{(9,8)} = 0.15$, $\beta^{(9,10)} = 0.10$, $\beta^{(10,9)} = 0.01$). The tenth well is much deeper than the others wells. After completion of the process $n_{10} = 0.66$ ($n_1 = 0.05$).

and 8 describe the opposite case where the well of each succeeding isomer in the chain (beginning with the second isomer) is more shallow than that of the preceding isomer. "Population transfer" from the initial to the final structure will still occur but the populations of the isomers of the chain will also retain, which will reduce the total efficiency of the process. Signal transmission and the final result also depend on the situation whether or not the pathway of the process passes through a rather deep single well capable of "trapping" a portion of the population.

Since we considered transmission of a signal along the chain of EES, for the process to complete none of the intermediate state should emit during the transmission time. This suggests that the most probable form of chain II transformations is a chain of triplet—triplet transitions. This implies that in the first stage a portion of energy should be nonradiatively transferred to the medium after a singlet—singlet photoexcitation. In this case, a vibrationally excited triplet electron state can be created as the initial state. The total spin state of the reaction products should be corresponding.

If the initial excitation occurs, for example, chemically, the process can involve only the ground states of the isomers. In this case, it seems more difficult to reach a deep well for the last isomer. That is why photochemical processes are preferential.

The method of signal transmission *via* "transfer" of the populations of isomeric states presented in this work can be named neither electronic nor vibrational. Indeed, although the overall process of consecutive isomerization is associated with large-amplitude vibrations, it is accompanied by the electron density redistribution (for example, multiple bond migration). No transfer of high electron density in the region of the double bond along the chain occurs; rather, the electron density disappears at one site and appears jumpwise at another site. Therefore, no analogy of this process to a continuous charge (electron) transfer along the chain can be drawn. The mechanism of signal transmission along the chain should be named vibronic and non-adiabatic because the eigenfunctions of the resonant doublets are non-adiabatic.

To maintain the quasi-stationary phototransformation resulting in the decomposition products of the terminal R unit of the ABR system, after the reaction ABR → AB + D + F (D + F = R) the R group has to add again to the AB fragment with recovery of the ABR structure. Therefore, the terminal unit of the AB fragment should play the role of a catalytic site capable of adding the R group, which is in the ground state as is the AB fragment, and, then, cleaving it after supply of energy from the photoacceptor.

Our model system A—CH=CH—$(CH_2)_n$—R (R = COOH) can undergo decarboxylation with CO_2 evolution (this reaction mechanism due to large-amplitude vibrations has been discussed earlier**[8]**), resulting in the —$CH=CH_2$ terminal group. Assuming that it is connected to a reservoir containing H_2O, O_2, and CO molecules, the recovery of the —CH=CH—COOH terminal unit is also quite possible.

Since isomerization involves migration of the double bond from the photoacceptor to the distant end of the chain, the transition of the ABR structure to the initial ground state (as it was before the act of light absorption) needs that the $(ABR)^{(1)}$ isomer be the lowest in energy. Then the system will spontaneously return to the most probable initial state due to the effect of the medium and the multiple bond will migrate in the opposite direction. Hence, we can assume the possibility of relatively easy temperature isomerization occurring due to internal rotations.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 01-03-32058).

References

1. V. A. Shuvalov, *Pervichnoe preobrazovanie svetovoi energii pri fotosinteze* [*Primary Light Energy Conversion in Photosynthesis*], Nauka, Moscow, 1990, 208 pp. (in Russian).
2. L. A. Gribov, V. I. Baranov, and D. Yu. Zelentsov, *Elektronno-kolebatel´nye spektry mnogoatomnykh molekul. Teoriya i metody rascheta* [*Vibronic Spectra of Polyatomic Molecules. Theory and Calculation Methods*], Nauka, Moscow, 1997, 475 pp. (in Russian).
3. L. A. Gribov and I. V. Maslov, *J. Mol. Struct.*, 2000, **521**, 107.
4. L. A. Gribov and I. V. Maslov, *Zh. Fiz. Khim.*, 2000, **74**, 441 [*Russ. J. Phys. Chem.*, 2000, **74** (Engl. Transl.)].
5. L. A. Gribov, *Zh. Fiz. Khim.*, 2001, **75**, 83 [*Russ. J. Phys. Chem.*, 2001, **75** (Engl. Transl.)].
6. L. A. Gribov, *Zh. Fiz. Khim.*, 2001, **75**, 290 [*Russ. J. Phys. Chem.*, 2001, **75** (Engl. Transl.)].
7. L. A. Gribov, *Zh. Fiz. Khim.*, 2001, **75**, 573 [*Russ. J. Phys. Chem.*, 2001, **75** (Engl. Transl.)].
8. L. A. Gribov, *Ot teorii spektrov k teorii khimicheskikh prevrashchenii* [*From the Theory of Spectra to the Theory of Chemical Transformations*], Editorial URSS, Moscow, 2001, **3**, 365 pp. (in Russian).

Received July 3, 2001