On the temperature dependence of the probability of structural interisomer transitions of molecules

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The properties of the intersection surface of the potential energy surfaces of structural isomers and kinetic characteristics of the reaction, including the physical meaning of the Arrhenius law parameters, are analyzed in detail. A number of corollaries important for determining the probability of the interisomer transition and the influence of the temperature factor on the probability and the pattern of this structural transformation were formulated. The theoretical model used describes the experimental regularities (Arrhenius law) and allows one to calculate the relevant parameters. The reason for manifestation of this regularity is the superposition of two factors, namely, the exponential dependence of the transition probability on the reciprocal temperature and the linear temperature dependence of the level of energy for which this probability is the highest.

Key words: isomerization, vibronic transition, Arrhenius law.

Structural isomer—isomer interconversions of complex molecules not accompanied by a change in their elemental composition induced by light (photochemical transformations) or by thermal excitation (thermal transitions) represent frequently encountered and important types of unimolecular reactions. In particular, they seem to play a crucial role in the transmission of signals and energy and in conversion and recording of the information in molecular systems.[1] Therefore, theoretical prediction of the probabilities and temporal characteristics of such structural transformations is a topical problem.

These items are widely discussed in the literature.[2—25] The unimolecular structural transformations are intensely studied by modern optical spectroscopy techniques with a high (pico- and femtosecond) temporal resolution.[11—17] Theoretical analysis carried out by quantum chemistry and molecular dynamics usually includes the study of the potential surfaces of molecular objects.[18—24] The temperature dependences of photoinduced and thermally induced intramolecular chemical processes are also studied.[11,25]

For molecular structures containing only 20 to 30 atoms, the number of isomers can reach tens of thousands, with interconversion of any isomer pair being theoretically possible. When the geometries of two isomers are appreciably different, direct transition between them can be forbidden (unlikely), but it can occur in several steps *via* a chain of isomer—isomer transformations, which can be very long and branched. This situation is typical in the solution of problems concerning intramolecular transport

of energy and signals by the vibronic mechanism.[1] It is quite evident that the traditional technique that implies the search for saddle points and routes for chemical transformations by calculating the characteristics of potential energy surfaces (PS) is practically inapplicable in this case. It appears promising to use the previously proposed approach,[26] which includes the solution of the spectral problem on energy levels of isomeric structures and the probabilities of optical or nonradiative transitions between them.

For nonradiative transformations, which we consider here, the transition between resonant ($E_{ev}^{(1)} \approx E_{ev}^{(2)}$) electronic-vibrational states of isomers 1 and 2 for a rather general external perturbation (for $t \geq 0$), occurs as beating of the mixed state

$$|\Psi(t)|^2 = 2a^2(t)[\psi_1^2\cos^2(0.5\Delta\omega t) + \psi_2^2\sin^2(0.5\Delta\omega t)] \qquad (1)$$

with the frequency $\Delta\omega = 2E_{ev}S_e^{(1,2)}S_v^{(1,2)}/\hbar$, determined by the magnitude of the corresponding off-diagonal element of the energy matrix, which characterizes the interaction of these isomeric states (environment, external field, *etc.*). The value $E_{ev} = 0.5(E_{ev}^{(1)} + E_{ev}^{(2)})$ is the average energy of the electronic-vibrational levels of the isomers and $S_{ev}^{(1,2)}$ is the overlap integral of the vibronic functions of the isomers. The transition time is determined by the beating period $t_{tr} = T/2 = \pi/\Delta\omega$ and the transition probability, by the value $w_{tr} = (1/t_{tr}) = (2/\pi\hbar)E_{ev}S_e^{(1,2)}S_v^{(1,2)}$. In expression (1), it is assumed that at the initial point in time ($t = 0$), the molecular system

Table 1. Calculated relative energies (ΔE) in the equilibrium states of structural isomers of the $C_{10}H_{18}O_2$ and $C_{20}H_{24}$ molecules

Isomer	$\Delta E/cm^{-1}$
$C_{10}H_{18}O_2$	
$H_2C=CH-(CH_2)_7-COOH$	0
$Me-HC=CH-(CH_2)_6-COOH$	−1200
$Me-CH_2-HC=CH-(CH)_5-COOH$	−970
$Me-(CH_2)_2-HC=CH-(CH_2)_4-COOH$	−1050
$Me-(CH_2)_3-HC=CH-(CH_2)_3-COOH$	−970
$Me-(CH_2)_4-HC=CH-(CH_2)_2-COOH$	−650
$Me-(CH_2)_5-HC=CH-CH_2-COOH$	−800
$Me-(CH_2)_6-HC=CH-COOH$	−650
$C_{20}H_{24}$	
$Me-HC=CH-(CH_2)_3-C_6H_6-HC=CH-Ph$	0
$Me-CH_2-HC=CH-(CH_2)_2-C_6H_6-HC=CH-Ph$	−80
$Me-(CH_2)_2-HC=CH-CH_2-C_6H_6-HC=CH-Ph$	−160
$Me-(CH_2)_3-HC=CH-C_6H_6-HC=CH-Ph$	0
$Me-(CH_2)_4-HC=C_6H_5-HC=CH-Ph$	−1770
$Me-(CH_2)_5-C_6H_4-HC=CH-Ph$	−8700

exists in the state corresponding to isomer 1. The overlap integral $S_{ev}^{(1,2)}$ is the key point in determining the probability of the interisomer transition because, depending on the difference between the isomer geometry, it can change by many orders of magnitude, while the E_{ev} value is mainly determined by the electronic energy and changes rather insignificantly from one isomer to another (see, for example, Table 1).

The first stage of simulation of interisomer transitions within the framework of this approach is the formation of adiabatic and harmonic models of the molecules corresponding to minima on the PS for each isomer; this can be easily done by known methods[27] using the corresponding databases.[28-30]

The second stage is to determine the conversion parameters for the normal coordinates of isomers

$$X^{(2)} = JX^{(1)} + g, \qquad (2)$$

namely the mixing matrix of the normal coordinates J and the shift vector (column matrix) for the PS minimum along the coordinate axes g, where $X^{(1)}$, $X^{(2)}$ are the column matrices of normal coordinates normalized to the amplitudes of zero-point vibrations ($X^{(1)} = Q_0^{(1)-1}Q^{(1)}$, $X^{(2)} = Q_0^{(2)-1}Q^{(2)}$; $Q_0^{(1)}$, $Q_0^{(2)}$ are the diagonal matrices for the zero-point vibration amplitudes). This problem can be easily solved by known methods.[31] The elements of the shift column vector g provide an immediate, rather rough estimate (according to the yes/no principle) of the probability of the transition between isomers 1 and 2. The known elements of shift vector g for a pair of isomers falling in the range of $5 \leq |g_i| \leq 15$ can be used as a criterion for selecting the possible isomer—isomer transitions

among the set of isomers of a molecular system with a specified elemental composition.

It can be demonstrated that transition to appropriately arranged reduced intrinsic coordinates, $Y^{(1)}$ and $Y^{(2)}$, which can be easily calculated, can totally eliminate the problem of calculating the electronic component of the total electronic-vibrational overlap integral $S_{ev}^{(1,2)}$ ($S_e^{(1,2)} \approx 1$), and the problem of determination of the transition probability w_{tr} can thus be reduced to the calculation of the Herzberg—Teller type vibrational overlap integrals $S_v^{(1,2)}$ with the weight coefficient of the form $Y_i^{(1)}Y_j^{(2)}$, which does not change the order of magnitude of the integrals with respect to the Franck—Condon integrals ($\langle v^{(2)}|v^{(1)}\rangle$) but changes only the corresponding quantum numbers $v_i^{(1)}$ and $v_j^{(2)}$ by unity. Thus, the ratio between the electronic and vibrational components of the general problem has actually changed with respect to that inherent in the approaches used previously and the main emphasis has been transferred from the electronic to vibrational part, which appears more physically sensible.

The overlap integrals $S_v^{(1,2)}$ can be easily calculated;[31] their change upon an increase in the quantum numbers $v^{(1)}$, $v^{(2)}$ (an increase in the energy level) follows a fairly characteristic pattern, namely, a nearly exponential build-up to the maximum value followed by relatively slight oscillations, which do not change the order of magnitude. The maximum is attained near the critical point of the PS of isomers, with the region of $S_v^{(1,2)}$ values significant in the order of magnitude being rather broad, namely, $\Delta v \sim 5$ (Fig. 1). By the critical point of the PS, we mean the point with the minimum energy on the multidimensional intersection surface of the PS of isomers. On the one hand, this describes the critical point as the most probable point for the isomer—isomer transition (which is correlated with its traditional interpretation as a passage through the saddle point of the PS), and, on the other hand, this shows the possibility of transitions with a rather high probability and at substantially lower excitation energies of the molecule.
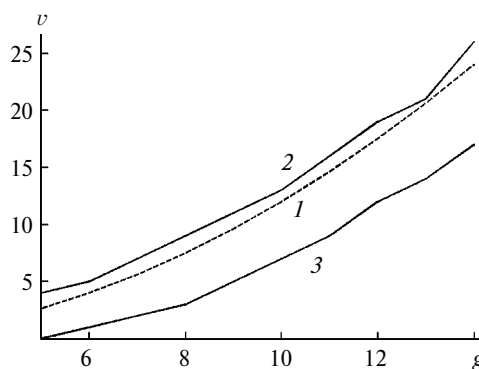

Fig. 1. Quantum numbers (v) of the vibrational levels of vibronic states corresponding to the critical point of the PS of isomers (*1*) and the maximum (*2*) and an order of magnitude lower (*3*) values of the overlap integral $S_v^{(1,2)}$ *vs.* the shift value g.

A significant role is played by the thermal distribution of molecules over the vibronic energy levels (see below). The harmonic approximation for the isomer models proves to be quite satisfactory because the energy levels are relatively low (the vibrational quantum numbers $v \leq 5$, see below) and the corresponding anharmonic contributions are small, on the whole, they are less than 10%.[32]

The importance of the PS critical point for the analysis of the interisomer transition stems from several factors. First, this point determines the most probable route for the structural transformation of isomers, as it lies (in the reduced coordinates) on the straight line connecting the minima on the PS of isomers and corresponding to the shortest distance between them, *i.e.*, this implies the minimum geometry change upon the isomer—isomer transition. Second, it gives the upper limit for the transition energy. Although this energy value may be markedly overestimated when the harmonic approximation is used, it can be easily corrected if required by applying appropriate anharmonic corrections.[32] Third, the position of this point shows what particular vibrations have to be excited for the transition to occur and, furthermore, indicates the type of these vibrations (overtone, combination vibrations), which enables an immediate rough estimate of the probability w_{tr}.

This study gives a detailed analysis of the properties of the intersection surface of the PS of isomers and the corollaries that are important for determining the probability of an interisomer transition and the effect of the temperature factor on the probability and the pattern of such structural transformation of a molecule. The kinetic parameters of the reaction including the physical meaning of the constants of the Arrhenius law are analyzed.

The critical point of the PS of isomers

For the harmonic model of molecules, the PS of isomers in the normalized normal $X^{(1)}$, $X^{(2)}$ coordinates are represented as

$$E^{(1)}(X^{(1)}) = \tilde{X}^{(1)}a^{(1)}X^{(1)} + E_0^{(1)}, \tag{3}$$

$$E^{(2)}(X^{(2)}) = \tilde{X}^{(2)}a^{(2)}X^{(2)} + E_0^{(2)}, \tag{4}$$

using the matrix form of notation (the energies and frequencies are expressed in cm^{-1} and the coordinates are in Å). The diagonal matrices $a^{(1)}$, $a^{(2)}$ contain the elements $a_{ii}^{(1)} = 0.5v_i^{(1)}$, $a_{jj}^{(2)} = 0.5v_j^{(2)}$, where $v_i^{(1)}$, $v_j^{(2)}$ are the vibration frequencies of isomers; and the $E_0^{(1)}$, $E_0^{(2)}$ values are the energies in the PS minima. Taking into account the conversion of coordinates (2) and the fact that $E^{(1)} = E^{(2)}$ at the points of intersection of isomer PS, we obtain the equation for coordinates (for example, of

isomer 1, $X^{(1)}$) located on the intersection surface of the PS of isomers

$$\varphi(X^{(1)}) = \tilde{X}^{(1)}(a^{(1)} - \tilde{J}a^{(2)}J)X^{(1)} - 2(\tilde{g}a^{(1)}J)X^{(1)} + C = 0. \tag{5}$$

The C constant is given by $C = \Delta E_0 - \tilde{g}a^{(2)}g$, and $\Delta E_0 = E_0^{(1)} - E_0^{(2)}$.

This second-order multidimensional equation always has a solution, except for the single case where the PS of isomers are "embedded" and have no intersection points. This case is of no interest, because we consider transitions between stable isomers of the molecule where the PS of a molecular system with a specified elemental composition contains two well-defined minima corresponding to two isomers and, hence, the PS of isomers are not "embedded" into each other. This entails certain constraints on the ΔE_0 value, which allow one to screen, already at this stage of modeling, the set of interisomer transitions possible for this molecular system and reject those of them that do not correspond to the problem in question.

Equation (5) in combination with expression (3) describes the intersection surface of the PS of isomers. The E_{ip}, $X_{ip}^{(1)}$ ($X_{ip}^{(2)}$) point corresponding to an energy minimum on this surface is found, in the general case, from the set of equations of the conditional extremum problem $\partial E^{(1)}/\partial X^{(1)} - \lambda \partial \varphi/\partial X^{(1)} = 0$, where λ are Lagrangian coefficients. This problem can be easily solved, for example, by nonlinear optimization methods. In addition, the problem can also be solved in an analytical form by switching to new, reduced coordinates $Y^{(1)}(Y^{(2)})$, in which the PS of isomers are paraboloids of revolution. To analyze the general regularities, it is more convenient to represent the intersection surface of the isomer PS in the normalized coordinates $X^{(1)}$ ($X^{(2)}$), because characteristics of molecular models in these coordinates are important for estimating and calculating the overlap integrals $S_v^{(1,2)}$ and, correspondingly, the transition probabilities w_{tr}.

Analysis of the overlap integrals $S_v^{(1,2)}$ (with allowance for their factorization property over normal coordinates with the required precision of estimates) shows that an interisomer transition is possible and most probable when one shift vector element g_i ($5 \leq |g_i| \leq 15$) can be distinguished, while the other elements are substantially smaller. The presence of two elements g_i and g_j that satisfy this condition markedly decreases the transition probability, although does not rule out completely the possibility of this transition. A larger number of elements of the vector g falling within this range makes the interisomer transition unlikely. This constitutes a criterion for rough rejection of isomer transitions according to the yes/no principle and shows that a more detailed quantitative analysis can be limited to transitions that are "one- or two-dimensional" regarding the transformation of normal coordinates. Note that this rejection of transitions and estimation of the "dimensionality" of the interisomer tran-

sition should be carried out based on the values of both the g vector, which specifies the shift of the minima of the isomer PS in the coordinates of isomer 2 ($X^{(2)}$), and the $J^{-1}g$ vector, which specifies the shift in the coordinates of isomer 1 ($X^{(1)}$). Thus, it is possible to take into account the normal coordinate mixing effect, which can be rather significant and, in particular, can give rise to cases where a one-dimensional transition in the coordinates $X^{(2)}$ would be multidimensional in the coordinates $X^{(1)}$. A two-dimensional case can be reduced to one-dimensional in the reduced normal coordinates with an appropriately corrected shift whose magnitude will not knowingly exceed $1.5\max\{g_i,g_j\}$. Hence, we restrict ourselves to considering a simple one-dimensional model.

For clarity, consideration will be limited to identical vibration frequencies of the isomers ($\nu^{(1)} = \nu^{(2)} = \nu$). In the absence of shifting of isomer PS along the energy scale ($\Delta E_0 = 0$), we have

$$X_{ip}^{(1)} = -0.5g, \tag{6}$$

$$E_{ip} = aX_{ip}^{(1)2} = 0.25ag^2 = 0.125\nu g^2. \tag{7}$$

Expression (7) gives the upper limit of the excitation energy of isomer 1 corresponding to the highest probability of its transition into isomer 2. The vibrational quantum number υ of the corresponding level can be estimated from the relation

$$\upsilon_{max} = [g^2/8 - 0.5], \tag{8}$$

where the brackets indicate that the integer part of the value is taken. The fast, quadratic increase in υ_{max} following an increase in g accounts for the upper limit of the range of possible values $5 \leq |g_i| \leq 15$ that enable the isomer transition over a practicable time.

Thus, determination of the shift vector g (which can be easily performed once the models of isomers 1 and 2 have been specified) provides a rough estimate of the possibility of this transition and allows one to elucidate the geometric transformation pathway ($X_{ip}^{(1)}$) and to find the upper limit of the excitation energies (E_{ip}) that corresponds to the highest transition probability and the corresponding quantum numbers (υ_{max}) of the overtone vibrational state. In turn, these quantum numbers can be used to estimate the probability of excitation of isomer 1 to the states needed for the interisomer transition.

In the presence of shifting of the isomer PS along the energy scale ($\Delta E_0 \neq 0$; Fig. 2), relations (6)—(8) are transformed to the form

$$X_{ip}^{(1)} = -0.5g + \Delta E_0/(g\nu) =$$
$$-0.5g[1 - 2\Delta E_0/(g^2\nu)] = -0.5g', \tag{9}$$

$$E_{ip} = 0.125\nu g^2[1 - 2\Delta E_0/(g^2\nu)]^2 = 0.125\nu g'^2, \tag{10}$$

$$\upsilon_{max} = [g'^2/8 - 0.5]. \tag{11}$$
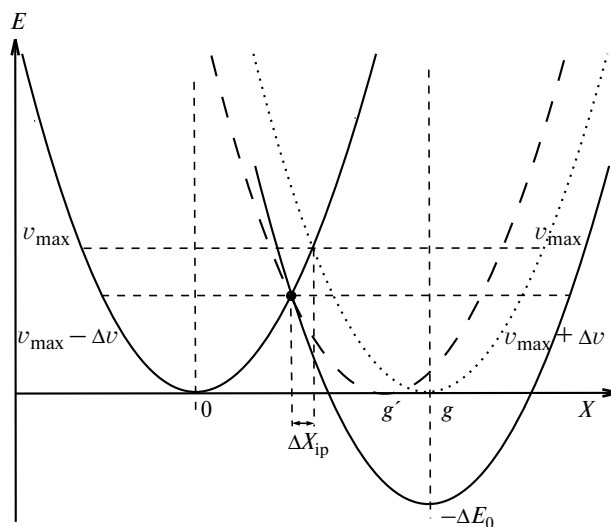

Fig. 2. Influence of the shift (ΔE_0) of the isomer PS along the energy scale.

Thus, the form of relations (6)—(8) obtained for $\Delta E_0 = 0$ and the estimates that follow from these relations do not change; one should only pass to the "effective" values of the shift vector

$$g' = g[1 - 2\Delta E_0/(g^2\nu)]. \tag{12}$$

At the critical point of the PS, the overlap integral $S_\nu^{(1,2)}$ changes insignificantly because it slightly depends on g. Therefore, the transition probability for the resonance (optical) excitation of an initial state close to E_{ip} changes insignificantly. It should be noted, however, that the excitation conditions are improved when $\Delta E_0 > 0$ because the energy E_{ip} decreases by a value of about $\Delta E_0/2$ and, correspondingly, υ_{max} also decreases. This can be easily seen in Fig. 2, which shows that the shift of the PS along the energy scale is equivalent, in terms of the position of the point E_{ip}, $X_{ip}^{(1)}$ and the $S_\nu^{(1,2)}$ value at this point, to the transition to the "effective" PS (dashed line) with the shift vector g changed in conformity with expression (12).

The effect of ΔE_0 on w_{tr} is most appreciable for the thermal population of the initial states of isomer 1 (see below), because not only does the energy E_{ip} decrease (when $\Delta E_0 > 0$) but also the PS for lower states ($E < E_{ip}$) come much closer to one another (see Fig. 2), thus increasing the overlap integrals $S_\nu^{(1,2)}$.

Characteristic features of the probabilities of the photochemical and thermal isomerization

The thermal distribution of molecules over the electronic-vibrational energy levels changes qualitatively the dependence of the transition probability, or, more pre-

cisely, the reaction rate constant k_{react}, on the quantum numbers v (or the energy E_v) of the "reactive" level with respect to resonance excitation. In this case, k_{react} includes also the Boltzmann factor and acquires the form

$$k_{react} = |S_v^{(1,2)}|\exp(-E_v/k_B T)E_{ev}/h, \qquad (13)$$

where E_{ev} is the electronic-vibrational energy of the isomer, which is approximately equal to the energy in the PS minimum, E_v is the energy of the vibrational ("reactive") sublevel, T is temperature, and k_B and h are the Boltzmann and Planck constants, respectively. The dependences of $|k_{react}|$ on v with allowance for the temperature for different shift vectors g are shown in Fig. 3 ($g = 8$ and 11), the variation of $|S_v^{(1,2)}|$ as a function of v is also shown for comparison (curve 5).
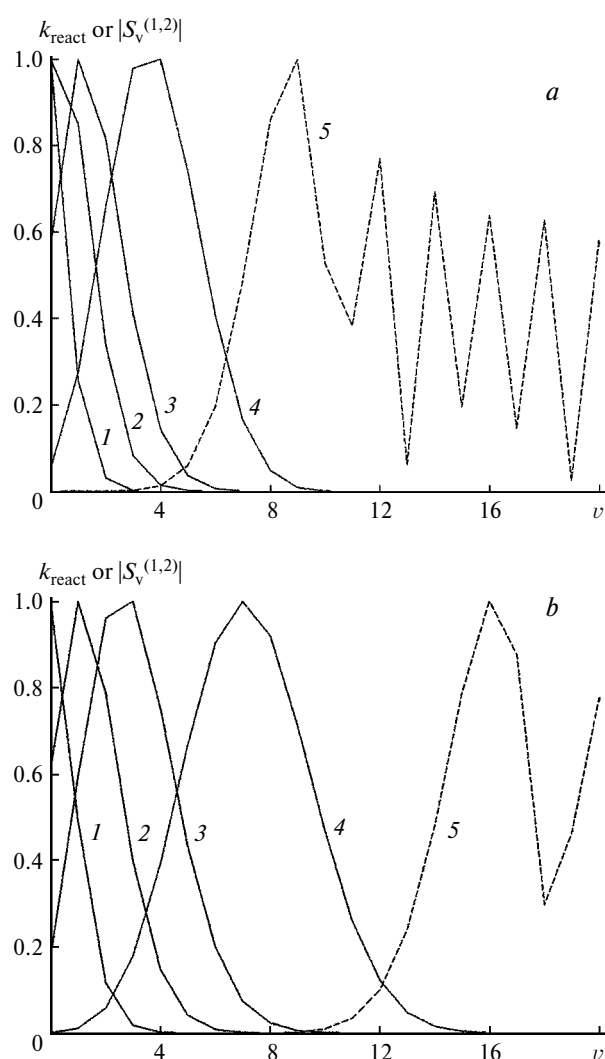

Fig. 3. Relative rate constants for the interisomer reaction (k_{react}) *vs.* quantum numbers v of the "reactive" level for $g = 8$ (*a*) and 11 (*b*) at different temperatures: 300 (*1*), 400 (*2*), 500 (*3*), and 800 K (*4*); $\nu = 1000$ cm^{-1}, $E_{ev} = 10^3$ eV. Curve 5 shows the dependence of the relative overlap integrals $|S_v^{(1,2)}|$ on v.

It can be seen that, unlike the nearly exponential increase of the integrals $|S_v^{(1,2)}|$ to the maximum followed by relatively small in magnitude oscillatory variation (see Fig. 3, curves 5), the dependence of $|k_{react}|$ on v with allowance for the thermal population has a clear-cut bell-shaped appearance, *i.e.*, out of the whole set of vibronic levels, a rather narrow group is cut (Δv is small; see Table 2) for which the probability of interisomer transition is the highest under the given conditions. Outside this group of levels, the transition probability rapidly decreases by an order of magnitude or more. The quantum numbers of the levels (v_{max}) characterized by the highest k_{react} values are appreciably smaller (by an order of magnitude at moderately elevated temperatures; $T \leq 500$ K) than those for the resonance excitation case and, generally, they are relatively small (for example, for $T \leq 500$ K, $v_{max} \leq 5$; see Table 2). Therefore, it is obvious that thermally induced interisomer transitions follow a clear-cut underbarrier (tunneling) pattern and occur through lower excited vibrational sublevels of electronic states. This is a distinctive feature of thermal reactions (compared to those initiated by a resonance optical excitation). In the latter case, however, one should bear in mind the fact that for complex molecules, the highest excitation probability is at-

Table 2. Reaction rate constants at the maxima of the $k_{react}(v,T)$ dependences, quantum numbers of the levels corresponding to the positions of these maxima (v_{max}), and the range of quantum numbers for which $k_{react} \geq 0.5 k_{react}^{max}$, ($\Delta v$) for different shifts ($g$) and temperatures ($T$)

g	T/K	Δv	v_{max}	k_{react}^{max}/s^{-1}
5	300	1	0	$8.5 \cdot 10^{13}$
	400	1	0	$1.5 \cdot 10^{14}$
	500	1	0	$2.2 \cdot 10^{14}$
	800	3	1	$7.2 \cdot 10^{14}$
8	300	1	0	$4.9 \cdot 10^{9}$
	400	2	0	$9.0 \cdot 10^{9}$
	500	3	1	$2.3 \cdot 10^{10}$
	800	4	4	$4.1 \cdot 10^{11}$
11	300	1	0	$3.2 \cdot 10^{3}$
	400	3	1	$9.5 \cdot 10^{3}$
	500	4	3	$4.7 \cdot 10^{4}$
	800	6	7	$1.2 \cdot 10^{7}$
13	300	1	0	$2.2 \cdot 10^{-2}$
	400	3	2	$9.2 \cdot 10^{-2}$
	500	5	4	$9.0 \cdot 10^{-1}$
	800	7	10	$1.8 \cdot 10^{3}$
15	300	2	0	$1.6 \cdot 10^{-8}$
	400	4	2	$1.4 \cdot 10^{-7}$
	500	6	5	$2.9 \cdot 10^{-6}$
	800	8	13	$6.9 \cdot 10^{-2}$
20	300	3	1	$2.7 \cdot 10^{-27}$
	400	5	5	$1.1 \cdot 10^{-25}$
	500	7	10	$2.3 \cdot 10^{-23}$
	800	10	24	$1.3 \cdot 10^{-15}$

tained when the quantum numbers of the combination states change slightly ($\Delta v \approx 0{-}2$).[31] Therefore, higher excited vibrational states are low populated, and the properties of thermal distribution would be largely transferred to the pattern of population of optically excited states by molecules, and, hence, to k_{react} (except for special excitation techniques, high power of laser radiation, $T \sim 0$ K and so on). This leads to the conclusion that the harmonic approximation is quite suitable for the modeling of interisomer transitions of complex molecules (the anharmonic corrections for the vibrational state energies never exceed[32] ~10%).

Only in the case where structural interisomer transitions characterized by shift vectors g close to the upper limit of the range of isomer—isomer transitions ($|g| \sim 15$) are accompanied by substantial geometry transformations and the temperature is very high ($T > 500$ K), we have $v_{max} > 5$, and anharmonic effects can be significant. They can be easily taken into account, if necessary, by introducing the corresponding anharmonic corrections (scaling factors), which are estimated by known methods.[32]

The k_{react} values at the maxima of $k_{react}(v, T)$ curves (see Fig. 3) are listed in Table 2. They change slightly with temperature for small shift parameters g ($g \sim 5$, $k_{react} \sim 10^{13}{-}10^{14}$ s^{-1} for $T = 300{-}800$ K). However, the whole range of possible variations of k_{react} as a function of temperature and the magnitude of structural deformations following an interisomer transition is rather broad, ~$10^{14}{-}10^{-8}$ s^{-1} for $T = 300{-}800$ K and $5 \leq |g_i| \leq 15$. The k_{react} values still remain rather high even for substantial structural transformations of the molecule; for example, for $g \sim 13$ (proton transfer in the allene—methylacetylene interisomer transition), $k_{react} \sim 10^{-2}$ s^{-1} even at room temperature, *i.e.*, the transition time is rather short, about 100 s.

This demonstrates, on the one hand, broad variability of interisomer structural transitions of molecules as regards their probability and time characteristics and, on the other hand, the applicability of our approach for fast evaluation of their values and for predicting the necessary and optimal conditions for particular isomer—isomer rearrangements.

Note that the analysis we performed confirms the earlier conclusion on the key importance of the shift parameter g for the quantities characterizing the probability of isomer—isomer rearrangements of molecules and the variation range $5 \leq |g_i| \leq 15$ (for $T = 300$ K and $g = 5$, 8, 11, 15, and 20, $k_{react} = 10^{14}$, 10^{10}, 10^3, 10^{-8}, and 10^{-27} s^{-1}, respectively).

For the shift values commonly observed for interisomer transitions ($g \sim 10{-}15$), the transition probability increases very rapidly with an increase in temperature, namely, by 0.5—1 orders of magnitude for $\Delta T = 100$ K. This reflects the typical "explosive" pattern of these reactions. The width Δv of the bell-shaped curve $k_{react}(v)$ increases with an

increase in T (for example, for $g = 11$, $\Delta v = 1{-}3$ at $T = 300{-}400$ K and $\Delta v = 4{-}6$ at $T = 500{-}800$ K), and the position of its maximum v_{max} ($v_{max} = 0{-}7$) shifts toward higher v. Therefore, the density of energy levels in the corresponding range of v also increases. This enhances the possibility of resonance of the levels of isomers 1 and 2 and makes more probable the transition through several resonating levels rather than through one level. Thus, the cumulative probability will grow even more rapidly with an increase in T than in the one-level situation and the "explosive" nature of this dependence will be even more pronounced. The more significant is the structural rearrangement of the molecule upon the transition (greater g values), the more pronounced is this feature.

Temperature dependence of the rate constants of thermal reactions

The time behavior of the populations of the electronic-vibrational states of isomers 1 and 2 (the numbers of molecules existing as these isomers) is described by a set of kinetic equations. We assume that the thermal equilibrium of molecules of each isomer (the thermal distribution over the energy levels) is established appreciably (an order of magnitude) faster than the transition of a molecule into an alternative isomeric form. In this case, the consideration can be restricted to a simple pattern of two resonating reactive levels, and transitions to states lower in energy can be taken into account by introducing a temperature factor for the population of the level of isomer 2 with respect to the level of isomer 1, namely, $\exp(-\Delta E_0 / k_B T) = \exp(-1.44 \Delta E_0 / T)$, where the energy is expressed in cm^{-1} and the temperature is in K. Indeed, for the populations n_{1v}, n_{2v} of the resonating vibrational sublevels $v^{(1)}$, $v^{(2)}$ of isomers 1 and 2, we have

$$\mathrm{d}n_{1v}/\mathrm{d}t = -wn_{1v} + wn_{2v},$$

$$\mathrm{d}n_{2v}/\mathrm{d}t = wn_{1v} - wn_{2v}.$$

Taking into account the thermal distribution $n_{1v} = n_1 \exp(-1.44 E_v^{(1)} / T)$ and $n_{2v} = n_2 \exp(-1.44 E_v^{(2)} / T)$, we obtain

$$\mathrm{d}n_1/\mathrm{d}t = -wn_1 + w\exp(-1.44\Delta E_0 / T)n_2, \qquad (14)$$

$$\mathrm{d}n_2/\mathrm{d}t = wn_1 - w\exp(-1.44\Delta E_0 / T)n_2, \qquad (15)$$

where n_1, n_2 are the numbers of molecules in isomer forms 1 and 2, and the probability of interisomer transition is determined by the beating frequency (1) and amounts to $w = \Delta\omega/2 = E_{ev}S_{ev}^{(1,2)}/\hbar$. Here, the probability values do not take into account the harmonic factor $\sin(2wt)$, which describes the beating process of the resonating states of isomers 1 and 2 and results in a harmonic "modulation" of the time dependences $n_1(t)$ and $n_2(t)$ with the frequency $2w$. In this case, modulation does not play
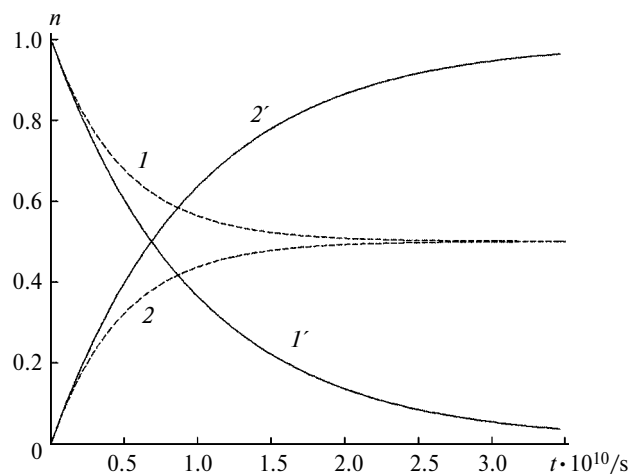
Fig. 4. Time variations of the number of molecules (*n*) in the isomer forms 1 (*1*, *1′*) and 2 (*2*, *2′*) at $\Delta E_0 = 0$ (*1*, *2*) and 1000 cm^{-1} (*1′*, *2′*). The probability of the interisomer transition $w = 10^{10}$ s^{-1}, $T = 300$ K.

any significant role. The form of kinetic equations, the probabilities of interisomer transitions, and characteristic features of the isomer—isomer rearrangements of molecules with allowance for quantum beatings will be considered in detail elsewhere.

The solution of the set of equations (14) and (15) for $\Delta E_0 = 0$ and $\Delta E_0 = 1000$ cm^{-1} ($T = 300$ K) is shown in Fig. 4. It can be easily seen that even at relatively low (~1000 cm^{-1}) ΔE_0 values, isomer 1 is almost completely (to 99%) converted into isomer 2, the concentration of the starting isomer $n_1(t)$ follows an exponential time dependence, and the reaction time corresponding to a ~2-fold change in the concentration depends not only on *w* but also on the parameter $\Delta E_0/T$, *i.e.*, on the temperature for the given pair of isomers.

This correlates with the Arrhenius law

$$k_A = A\exp(-E_a/k_B T), \tag{16}$$

where *A* is the absolute rate of the chemical reaction and E_a is the activation energy, especially in view of the fact that the above-introduced constant for the isomer—isomer transition with allowance for the thermal distribution of molecules over the energy levels (13) is equal to

$$k_{react} = w_v\exp(-E_v/k_B T), \tag{17}$$

where w_v and E_v are the transition probability and the energy of the reaction level (corresponding to the highest w_v). Moreover, the variation of $\ln k_{react} = \ln w_v - E_v/k_B T$ *vs.* $1/T$ is nearly linear (Fig. 5), as in the case of the Arrhenius law (16).

This formal full analogy in appearance, which at first glance implies the equivalence (or identity) of the *A* and w_v values and the E_a and E_v values, contains an inherent contradiction lying in the fact that the parameters of the
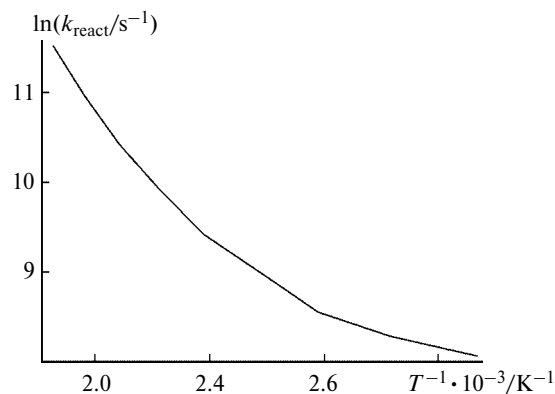

Fig. 5. Reaction rate constant (k_{react}) *vs.* temperature; $g = 11$, $v = 1000$ cm^{-1}, $E_{ev} = 10^3$ eV.

Arrhenius law (16) are constants, whereas the w_v and E_v values appearing in relation (17) depend (as shown above, to a large extent) on the temperature.

Now we consider this item in more detail.

The dependence of v_{max} on *T* can be described with high accuracy by a linear function of the form

$$v_{max} = v_0 + \beta T. \tag{18}$$

Indeed, for example, for $g = 11$, the parameters $v_0 = -5$ and $\beta = 0.015$ K^{-1} provide full coincidence of the v_{max} values calculated using relation (18) with those listed in Table 2 over a broad temperature range ($T = 300$—800 K). Similar results are also obtained for other values of the shift parameter *g*. This means that the energy E_v also depends linearly on *T*:

$$E_v = \varepsilon_0 + \beta_0 T, \tag{19}$$

where $\varepsilon_0 = hcv(v_0 + 1/2)$, $\beta_0 = hcv\beta$, *v* is the active vibration frequency, *c* is the speed of light (in expression (16) and subsequently, we do not pass to energy characteristics in cm^{-1}).

The dependence of the overlap integrals $S_v^{(1,2)}$ on *v* is nearly exponential (Fig. 6); therefore, taking into account Eq. (18), we get

$$w_v = a\exp(-\alpha/k_B T). \tag{20}$$

Then the expression for the reaction rate constant (17) acquires the form that exactly coincides with the Arrhenius law (16):

$$k_{react} = w_v\exp(-E_v/k_B T) = A\exp(-E_a/k_B T), \tag{21}$$

where $A = a\exp(-\beta_0/k_B)$, $E_a = \alpha + \varepsilon_0$, and these values are constants. Thus, the absolute rate of the reaction *A* present in the Arrhenius law, which shows the reaction rate at $T = \infty$ (*i.e.*, in the case of uniform distribution of molecules over energy levels), is determined by the parameters *a* and β_0, the former representing the transition probability w_v at $T = \infty$ and the latter corresponding to the
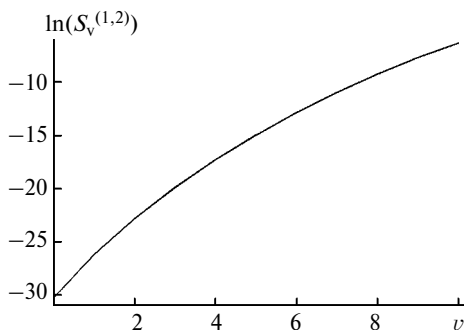
Fig. 6. Overlap integrals $S_v^{(1,2)}$ *vs.* quantum numbers v for $g = 11$.

energy change for the "reactive" level E_v following a one-degree change in the temperature. The activation energy E_a, equal to the change in the reciprocal temperature (in energy units) that induces a change in the reaction rate by a factor of e, is determined by two addends, α and ε_0: the former shows the change in $(k_B T)^{-1}$ (the corresponding w_v value changes e-fold), while the second gives the "pseudo-level" energy (for which the highest reaction rate constant is observed when $T = 0$).

It can be seen that the parameters a and α are analogous in the physical sense to the parameters A and E_a, while ε_0 and β_0 give corrections associated with the temperature variation of the E_v level most efficient for the reaction. It is the characteristic form of the variation of w_v and E_v with temperature (19) and (20) that results in the Arrhenius law for the temperature dependence of the reaction rate constant (16).

Thus, this theoretical model describes the experimentally observed regularities (Arrhenius law), makes it possible to calculate the characteristic parameters (A and E_a), establishes the factors responsible for manifestation of this feature, namely, the superposition of two factors: an exponential dependence of the transition probability on T^{-1} and the linear temperature dependence of the energy level where this probability is maximum on T.

$$* \qquad * \qquad *$$

The interpretation of kinetic equation parameters (reaction rate constant, activation energy) is different for photo processes (resonance excitation, supersonic stream, nonthermal level distribution) and for thermal chemical isomer—isomer transformations of molecules.

In the case of photo processes with single-level excitation (dispersion spectroscopy), the Arrhenius law is not valid. The activation energy is the energy of the level to which photoexcitation occurs and for which the probability of nonradiative interisomer transition is high. It corresponds to the level at the PS critical point or to a close level (the probability of transition is maximum) and is the analog of the barrier energy in the transition complex theory. The key activation parameter of the transition

upon this type of excitation is the energy level at the critical point of the isomer PS.

In the case of thermal interisomer transitions, the dependence of the transition probability on the energy level is bell-shaped and has a clearly defined and a rather narrow maximum, which lies substantially lower (often by an order of magnitude) than the critical point of the isomer PS. The energy of the level corresponding to this maximum should be regarded as the activation energy. The thermally induced interisomer transition follows an "underbarrier" (tunneling) pattern. The process kinetics is described by the Arrhenius law whose parameters change only slightly with temperature, due to the effect of two factors, namely, the nearly exponential increase in the transition probability and the linear increase in the energy of the corresponding level with an increase in temperature.

The low energy of the "reactive" level in the thermal processes shows a high degree of applicability of harmonic models of isomers for modeling these processes.

Upon a usual nonresonance optical excitation of complex molecules, the thermal distribution of the initial state over the levels is transferred with a high degree of accuracy to photoexcited states. Therefore, the energetic and kinetic features of such an interisomer transformation of the molecule are the same as those of thermal processes.

This analysis and the results obtained can be extended to bimolecular reactions by transforming the vibrational functions of the electronic-vibrational states taking into account the translational component for a pair of reactants.

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