# Full Articles

## On the theory of processes in reaction centers of polyatomic molecules

*L. A. Gribov,* V. I. Baranov, and V. A. Dement´ev*

*V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, 19 ul. Kosygina, 119991 Moscow, Russian Federation*
*Fax: +7 (495) 938 2054. E-mail: gribov@geokhi.ru*

Based on general principles of quantum theory of chemical transformations for polyatomic molecules, the notion of the reaction center (RC) was revised. The presence of RCs is a necessary condition for occurrence of all types of chemical transformations in complex systems. The physical picture of processes in RCs, conditions for maximum probability of transformations, the local character of a chemical reaction and its relation to the characteristic vibrations, and the methods of *a priori* search for RCs based on normal coordinate analysis of coupled states and on calculations of overlap integrals between vibrational wave functions were studied. Specific features of manifestation of characteristic vibrations in vibrational and vibronic spectra were investigated and the possibility of search for RCs using optical spectroscopy was considered.

**Key words:** chemical transformations, reaction centers, characteristic vibrations.

Description, interpretation, and prediction of structural transformations of complex molecules upon thermal or optical excitation (thermally induced and photochemical transformations, respectively) belong to the key problems in chemistry. They have long been a subject of considerable literature. Intensive experimental (by, *e.g.*, high-resolution femtosecond spectroscopy[1—7]) and theoretical (mainly by quantum chemical and molecular dynamics methods based on the study of the potential energy surfaces (PESs) of molecules[8—14]) research has also been carried out. The theoretical approach to the determination of pathways of chemical transformations involving search for saddle points on the PESs of various molecules seems to be of limited use. The reasons are as follows. The approach provides no information on the dynamics and, hence, temporal parameters of processes under study and on their probabilistic characteristics. As a consequence, the concentrations of products cannot be determined. The activation energy for the process is defined as the energy of the saddle point, although a tunnelling process (*i.e.*, under-barrier transition) is highly probable (and even typical),[15—18] the notion "transition state" corresponding to the saddle point is conditional, *etc*.

At the same time, a general theory of chemical transformation is developed. It is based on a new approach, which treats molecular transformations as resonant transitions between levels and states of a molecular structure and is a natural continuation and development of the

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1267—1273, August, 2006.

1066-5285/06/5508-1315 

theory of spectra.[19] Here, molecular transformations are described with allowance for the intra-isomer and isomer-isomer optical transitions and the transitions corresponding to bimolecular reactions. The intra-isomer transitions occur between states of a given isomer of a molecule, whereas the isomer-isomer transitions occur between states of different isomers of a given molecule. The possibility of developing such a theory was first reported by B. I. Stepanov who formulated the general idea of the approach in a study with a remarkable title "On identity of methods for description of chemical and spectroscopic processes".[20]

The key features of a theory that correctly describes processes occurring in the nature are reproduction, prediction, and explanation for the majority of experimental data using a few basic principles. In the framework of the theory being developed this was done for a number of key experimental relationships including the following[21–34].

1. Periodic changes in the intensities of spectral lines due to the effect of quantum beats against the background of the overall temporal evolution observed at very short durations of excitation pulses.

2. Strong (even on the qualitative level) differences between the temporal dependences of the intensities of particular spectral lines.

3. Delayed development of the spectral picture due to the dynamics of photoisomerization processes.

4. High sensitivity of the accumulation of isomers and their final concentrations upon photoisomerization to specific structural features of the molecular system under study and experimental conditions.

5. The Arrhenius law for thermally induced reactions, manifestation of an induction period of a chemical reaction, temporal dependence of the rate constant for a chemical reaction, and an S-like shape of the corresponding plot under particular conditions.

This indicates workability and high predictive power of this theory.

It is well known that in complex systems significant changes in the mutual position of atoms in reaction products compared to the initial reagents (physically, this is a chemical transformation) occur locally. Reactions involving a rearrangement of the whole molecule are hardly probable. This observation is substantiated by the vast majority of data obtained in various chemical experiments. It led to introduction of the notion "reaction center" (RC) as one of the basic notions in chemistry.[35] Nevertheless, the theory of chemical transformations provides no substantiation of this notion and no means for analysis of the necessary and sufficient conditions for the presence of RCs and specific features of the processes occurring in them based on the basic principles of quantum theory without using empirical information, *i.e.*, from *the first principles*. This is one of the key problems in chemistry and, moreover, this is a subject of the present study.

We will begin analysis of the necessary and sufficient conditions for the presence of RCs with substantiation of a local character of chemical transformations using no data obtained in chemical experiments. Then, we will consider the properties of RCs based on the results of model calculations of isomer-isomer transitions in molecular systems (mainly [1,3]-sigmatropic proton shifts and related consecutive reactions). In conclusion we will dwell on the role of characteristic features of vibrations as a necessary condition for the possibility of a chemical transformation in a reaction center.

## Local character of chemical transformations

Consider three most characteristic types of chemical reactions, namely, isomerization ($A \rightarrow A^*$), addition ($A + B \rightarrow C$), and decomposition ($A \rightarrow B + C$). Here the asterisk denotes an isomer. More complex reactions of the type $A + B \rightarrow C + D$ should involve the formation of intermediate (probably, short-lived) structures F and F*, that is, $A + B \rightarrow F \rightarrow F^* \rightarrow C + D$ (or a series of consecutive reactions $A + B \rightarrow F \rightarrow F^{**} \rightarrow \ldots \rightarrow F^* \rightarrow C + D$ if structural deformation corresponding to the transformation $F \rightarrow F^*$ is too large). According to calculations,[34] this chain-type transformation can result in very low fractions of intermediate structures (an example is provided by the double bond migration along the paraffin chain). For instance, a consecutive isomerization of phenylheptadiene (Scheme 1) at particular ratios of transition probabilities between different levels is characterized by the formation of isomer **4** as the major product (~70%) and by low fractions of the initial (**1**) and intermediate (**2**, **3**) isomers (~10%, Fig. 1).

It should be noted that the initial stage of the decomposition reaction can be treated as an analog of structural isomerization. Indeed, here the action of external factors on a rather stable initial molecule A led to formation of loosely bound fragments that will give rise to two different structures, B and C, in the next stages of

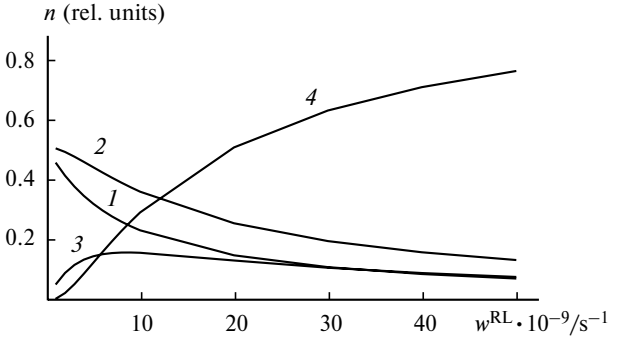
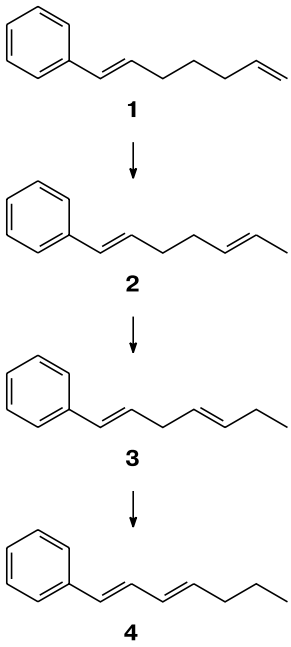



**Fig. 1.** Final ground-state fractions ($n$) of phenylheptadiene isomers **1** (*1*), **2** (*2*), **3** (*3*), and **4** (*4*) (see Scheme 1) plotted *vs.* probabilities ($w^{RL}$) of intra-isomer optical transitions between the coupled levels.

**Scheme 1**




decomposition. This was named "pre-decomposition" isomerization.[19] Therefore, now we will consider structural isomerization. This simplifies our treatment, makes it clearer, but does not restrict the general character of conclusions.

If changes in spatially localized molecular systems containing the same atoms manifest themselves as isomer-isomer structural transformations, they can be interpreted as transitions between energy levels and states of the same system. It is this approach, namely, treatment of molecular transformations as transitions between levels and states of a molecular structure is basic to the theory being developed.[19] The transition probabilities are given by corresponding off-diagonal elements of the energy matrix, which are proportional to the overlap integrals $S$ of the eigenfunctions of the coupled states. Indeed, the probability ($w$) of a nonradiative transition between coupled states of isomers (different structural forms of a molecular system) is proportional to the frequency ($\omega$) of quantum beats between these states $\omega = 2\hbar^{-1}E_{ev}S$, where $E_{ev}$ is the total energy of a given vibronic state.[29] The wave functions corresponding to particular isomers are localized in particular domains of the multidimensional coordinate space. Clearly, if the centers of these domains are separated by rather long distances, the integrals and the matrix elements mentioned above are small and, therefore, the transition probabilities are also low.

This suggests the existence of "spatial" forbiddenness on the course of both simple isomerization reactions and other types of reactions. Indeed, let us introduce a generalized geometric characteristic of a structural deformation of a molecule upon a chemical transformation (in particular, isomerization) and find how the probability of this transformation is related to the deformation. Note that any structural (geometric) state of a molecular system corresponds to a point in the space of certain generalized coordinates and any molecular transformation can mathematically be described as a transition between two points in this space provided conservation of the overall atomic composition. Without restriction of generality the distances between pairs of atoms (assuming that all atoms are enumerated and the atomic numbering scheme remains unchanged in the course of reaction), the angles between portions of the straight lines connecting pairs of atoms chosen in such a way that they share an atom (vertex of the angle), the corresponding dihedral angles, *etc*. can be used as the generalized coordinates provided that the overall atomic composition remains unchanged. For the starting reagent, this system of coordinates coincides with the system of natural coordinates. Differences between the spatial structures of isomers will be characterized in the system of normal coordinates for one of them by introducing the (dimensionless) shear vector normalized to the zero-point vibrational amplitudes[19,36–38]

$$b = Q_0^{-1}\tilde{L}_p q, \qquad (1)$$

which is linearly related to the changes in the geometry in the system of natural coordinates $q$ (changes in the interatomic distances, angles, *etc*.). Here $Q_0$ and $L_p$ are the matrix of zero-point vibrational amplitudes and the matrix of conjugated momenta, respectively. These matrices can always be defined unambiguously and calculated for an isomer chosen using methods of the theory of molecular vibrations.[39] Differences between the geometric parameters of the molecular structures **1**, **2**, *etc*. and a given structure are quantitatively characterized by the norms (lengths) of the vectors $b$ ($\|b_1\|$, $\|b_2\|$, *etc*.). Note that the vector $q$ and, hence, its norm $\|q\|$ can only be used for qualitative rather than quantitative comparison because the elements of this vector correspond to geometric coordinates of different types. The choice of the vector $b$ for characterization of the differences in the geometric configurations of molecular structures is also due to the fact that it determines the numerical value of the overlap integral, especially if the molecular structure is deformed largely.[29,33] The $S$ values and, hence, the corresponding matrix element characterizing the transition probability is proportional to $\exp(-b^2)$ and therefore rapidly decreases as $\|b\|$ increases (*e.g.*, it decreases by two orders of magnitude as $b^2$ varies from 1 to 5).[40]

It is of crucial importance, especially for preliminary estimation of the probability of the reaction under study, that the $b^2$ value can be determined with a reasonable accuracy without solving the vibrational problem for the

structures being coupled. Indeed, taking into account expression (1), we get

$$b^2 = \|b\|^2 = \tilde{q}L_pQ_0^{-2}\tilde{L}_pq \cong \overline{Q}_0^{-2}\tilde{q}L_p\tilde{L}_pq = \overline{Q}_0^{-2}\tilde{q}T^{-1}q, \quad (2)$$

where the diagonal matrix $Q_0^{-2}$ is replaced by its approximate representation $Q_0^{-2} \cong \overline{Q}_0^{-2}I$, where $\overline{Q}_0^{-2} = \left[\sum_{i=1}^{N}(Q_0^{-2})_{ii}\right]\Big/N$ is the average value of the elements of the matrix $Q_0^{-2}$, $I$ is the unit matrix, $N$ is the dimensionality of the matrix (since the numerical values of the $(Q_0^{-2})_{ii}$ elements differ insignificantly, this approximate representation *a priori* does not change the order of magnitude of $b^2$); $T^{-1}$ is the kinetic energy matrix of the molecule, which is expressed in velocities[39] ($T$ is expressed in momenta), being therefore symmetrical and positively defined. Then, using an orthogonal transformation $q = Dq'$ with conservation of the lengths ($\|q\| = \|q'\|$), the matrix $T^{-1}$ can be diagonalized, all elements of the diagonal matrix $\Lambda = \tilde{D}T^{-1}D$ being positive ($\lambda_i > 0$), and one gets

$$b^2 \cong \tilde{q}'\Lambda q'. \quad (3)$$

It follows that when considering the probabilities of isomerization of the initial molecular structure to structures **1**, **2**, **3**, *etc.*, it is sufficient to calculate $\Lambda$ for the initial structure (this can be done with ease and requires only knowledge of the geometric parameters) and to determine the values $b_1^2$, $b_2^2$, $b_3^2$, *etc.*, from relationship (3). These values will allow one to distinguish one or a few most possible structural transformations that correspond to the maximum $b_i^2$ values.

An increase in the structural deformation in the system of natural coordinates leads to an increase in the norm of the vector $\|q\|$ and, hence, to an increase in $\|q'\|$, $q_i'$, and $b^2$. In this sense the parameters $q^2$ and $b^2$ are equivalent and both of them can be used for characterization of the structural deformation in the molecule in the course of isomerization. Nevertheless, it is more preferable to use the $b^2$ parameter because the vector $b$ corresponds to the normal coordinates (*i.e.*, to the same-type coordinates) and is responsible for the numerical value of the overlap integral.

The $b^2$ value can be large if the reaction is characterized by a great change in the interatomic distance for a pair of atoms (*e.g.*, of the order of 5 Å and more) and if many coordinates vary simultaneously, although to a lesser extent (of the order of at most 0.5 Å). The latter case is characteristic of the "skewed" transitions that are much less probable for complex molecules than typical purely optical transitions for which the natural coordinates vary within relatively narrow ranges (of the order of 0.01 Å for the bond lengths and 1° for the bond angles) upon excitation and $\|b\|$ is of the order of unity.[36—38]

Chemical transformations correspond to atomic rearrangements accompanied by considerable changes in the interatomic distances (typically, of the order of 1.5—3 Å) and angles; therefore, they can only be local in character and involve a small number of atoms. Otherwise, the probabilities of direct chemical transformations of complex molecules should be negligible.

Indeed, the overlap integrals for the coordinates corresponding to large elements of the shear vector ($|b_i| \geq 5$) and determining the rearrangement in the isomer were estimated at $|S| \approx 0.15$—$0.1$.[29,33] If the changes in the coordinates upon isomerization are similar to their changes upon intra-isomer vibronic transitions ($0 \leq |b_i| \leq 2$), the overlap integral approaches a unity, although the scatter is much larger ($0.3 \leq |S| \leq 1$). An important consequence following from this is qualitatively understandable from general physical considerations and was already mentioned above. Assuming that all elements of the shear vector are larger than 2, which corresponds to a large deformation of the whole molecule, all one-dimensional components of the total overlap integral are of the order of $10^{-1}$ and the numerical value of this integral will decrease as a power function, $|S| \sim 10^{-N} \approx 10^{-3N_{at}}$ ($N$ and $N_{at}$ are respectively the number of normal coordinates and the number of atoms in the molecule), with an increase in the dimensionality of the problem in question. As the molecule becomes larger, its energy also increases ($E_{ev} \sim N_{at}$), but the numerical value of the overlap integral decreases much faster. Therefore, the probability of an isomer-isomer transition corresponding to a large deformation of the whole molecule is negligible even for relatively small molecules.

Thus, the local character of structural transformations involving a relatively small molecular fragment is the key factor responsible for the probability of a given isomer-isomer transition.

Clearly, very large structural transformations of molecules can only occur as a result of a sequence of independent steps, each of them corresponding to a local deformation. This also provides an explanation for the impossibility of direct transformation A + B → C + D (see above).

## Properties of reaction centers

Consider the properties of RCs taking model calculations of isomerization of rather simple molecular systems as examples. The matrices of transformation of the normal coordinates upon isomerization, the corresponding overlap integrals between the vibrational wave functions, and the frequencies of quantum beats corresponding to the isomer-isomer transitions were calculated.[19,29,33] The last-mentioned parameters appear in the kinetic equations that describe the population dynamics of the energy levels of the isomers and characterize the duration of the

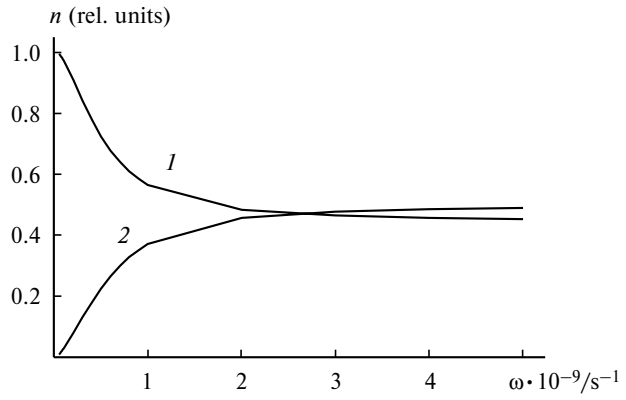



**Fig. 2.** Final ground-state fractions ($n$) of phenylheptadiene isomers **1** (*1*) and **2** (*2*) (see Scheme 1) plotted *vs*. frequency of quantum beats of the coupled levels (ω).

transition between the coupled (resonant) states of the isomers of the molecular system[31] and, hence, indirectly (similarly to the $b$ values) characterize the probability of the isomer-isomer transition. For instance, the fraction of the final isomer increases while that of the initial isomer decreases as the frequency of quantum beats increases (Fig. 2).

Now we will consider the characteristics of isomerization of particular molecules in which the elongating chain segment with ordinary bonds is linked to the same fragment in which structural rearrangement occurs in the course of isomerization. These are the but-1-ene ⇌ but-2-ene, hex-1-ene ⇌ hex-2-ene, oct-1-ene ⇌ oct-2-ene, and dec-1-ene ⇌ dec-2-ene isomerizations (Scheme 2).

**Scheme 2**

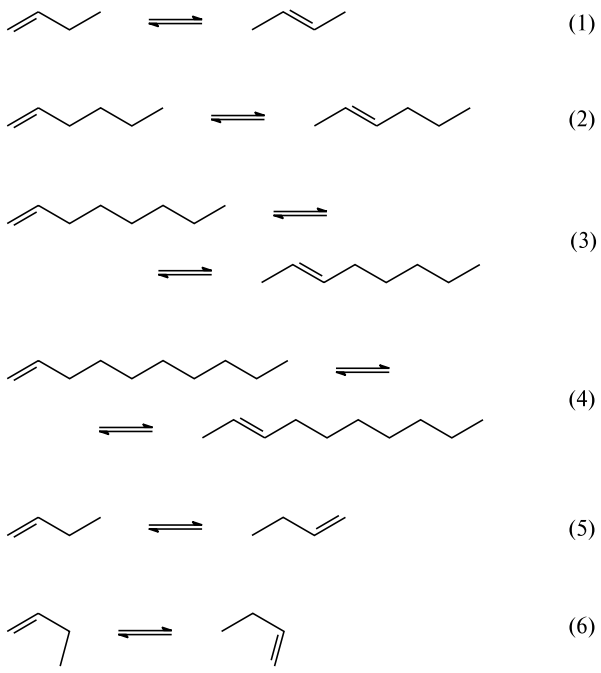



**Table 1.** The norms of the shear vectors ($\|b\|$), relative absolute values of overlap integrals of the wave functions for coupled levels ($|S|$), and quantum beat frequencies (ω) for isomer transitions of alkenes

| Isomer transition | $\|b\|$ | $\|S\|$ | ω |
|---|---|---|---|
| | | rel. units | |
| (1) | 20 | 1 | 1 |
| (2) | 20 | $1 \cdot 10^{-2}$ | $1 \cdot 10^{-2}$ |
| (3) | 20 | $1 \cdot 10^{-3}$ | $1 \cdot 10^{-3}$ |
| (4) | 20 | $1 \cdot 10^{-3}$ | $1 \cdot 10^{-3}$ |
| (5) | 22 | $1 \cdot 10^{-4}$ | $1 \cdot 10^{-4}$ |
| (6) | 18 | $1 \cdot 10^{-2}$ | $1 \cdot 10^{-2}$ |

Here, we deal with similar-type structural deformations in the course of isomerization. The deformation is spatially localized and therefore has a constant magnitude characterized by the norm of the vector $b$ ($\|b\| \approx 20$; Table 1); however, the numerical values of the elements of the corresponding vectors $b$ vary (Fig. 3). The number of the large elements of the vector $b$ ($b_i \geq 5$) is 7, 5, 4, and 4 for the butene, hexene, octene, and decene molecule, respectively. Small (compared to the total number of the elements of the vector $b$) variations of the number of the large elements for this group of molecules are related to small changes in the eigenvectors of vibrations. This in turn causes changes in the numerical values of the overlap integrals between the vibrational wave functions for the coupled levels and, as a consequence, similar (in order of magnitude) changes in the frequencies of quantum beats (see Table 1). Noteworthy is that the largest changes in $|S|$ and ω (*i.e.*, by an order of magnitude) occur only for small molecules. It is of crucial importance that these changes for the molecules in question are rapidly "saturated" and further elongation of the molecular chain

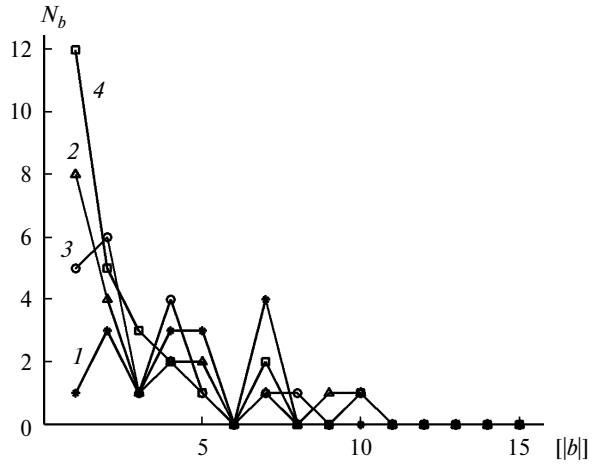



**Fig. 3.** Structures of $b$ vectors for isomer transitions (1)—(4) (see Scheme 2) (*1—4*, respectively ); $N_b$ is the number of elements of vector $b$ equal to $[|b|]$ ($[x]$ is the integer part of $x$); the number of zero elements of the vector $b$ is 13, 24, 40, and 49, respectively.

has a little effect on the key characteristics of isomerization.

Thus, the local properties of the RCs vary insignificantly. This means that the RCs are to a great extent independent of the molecular environment.

Noteworthy is that the probability of the transition but-1-ene ⇌ but-3-ene (see Scheme 2, Eq. (5)) involving migration of the C=C bond through one bond is much lower than the probability of the transition but-1-ene ⇌ but-2-ene. Namely, the corresponding $|S|$ and ω values decrease by four orders of magnitude (see Table 1). We can state that the principle of short-range action, which is basic to physics, also holds for chemical transformations. Long-range transmission of a signal in the form of structural deformation is only possible if it involves intermediates, *i.e.*, occurs by the chain mechanism *via* intermediate isomeric forms.

Yet another important example is as follows. It was reported[19] that transformation of linear hydrocarbon isomers to T-shaped ones is possible due to the fact that appropriate atoms approach one another in the course of internal rotation in molecules, which results in the appearance of the RCs. This conclusion is confirmed by the calculations of the $|S|$ and ω values for the transformation of the "linear" and "bent" isomers of but-1-ene to but-3-ene (see Scheme 2, Eqs (5) and (6)). If in the former case the migration of the double bond through one ordinary bond is almost forbidden, in the latter case the distances to be travelled by the corresponding hydrogen atoms are much shorter. As a consequence, the $\|b\|$ value decreases and the $|S|$ value and, hence, ω increases by two orders of magnitude (see Table 1).

### Purity of vibrations of the reaction center

Now we will consider yet another significant factor. Since vibrations represent the most important form of the relative motion of atoms in molecules, any chemical transformation can occur only involving vibrations, namely, highly excited ones. Changes in the relative atomic positions in molecules manifest themselves in the changes in the natural coordinates $q$ that are related to the normal coordinates $Q$ as follows: $q = L_q Q$. If only one normal vibration (*e.g.*, $k$th vibration; $Q_j = 0$ at $j \neq k$) is excited, the changes in the natural coordinates are determined by the elements of the $k$th column of the eigenvector matrix $l_q^{(k)}$ ($q_i^{(k)} = l_{qi}^{(k)} Q_k$). It is also well known[39] that the higher the degree of coupling of the normal vibration the larger the number of non-zero elements in the column $l_q^{(k)}$ and the smaller their values. Therefore, it is clear that typical "spectroscopic" and "chemical" energies can be used to excite the desired large-amplitude vibrations only provided that these vibrations are local in character or they can be considered pure in the region where the chemical transformation occurs. Note that only a few vibrations meet these conditions.

These conclusions are substantiated by the results of qualitative (visual) analysis of calculated atomic vibrations in coupled isomers for numerous well-known reactions.[19,21–26] In all cases, two or three characteristic vibrations corresponding to structural transformations in the course of isomerization were clearly seen. This can also be seen from the estimated magnitudes of the elements of the shear vectors for alkene molecules (see text above and Fig. 3). Yet another example is provided by the allene—metylacetylene transition. This is the case of a small molecule ($N_{at} = 7$, $N = 15$), but two vibrations responsible for the corresponding atomic rearrangement involving transfer of a proton can be distinguished. These are the C—H stretching vibration and the C—C—C bending vibration (the corresponding frequencies $\nu_i$ are about 3000 and 300 $cm^{-1}$). The responsibility of these vibrations for the isomerization manifests itself in the elements of the shear vector, namely, $|b_i| \approx 13$. The magnitude of the norm of the vector $b$ is mainly determined by these elements. The elements of the vector $b$ for other vibrations are much smaller.

Thus, analysis and model calculations showed that the crucial role in determining the possibility (*i.e.*, relatively high probability) of a certain structural transformation of a molecule is played by not only the local character of the structural transformation, but also the corresponding characteristic vibrations. These are the key requirements.

It is very important that specific features of atomic motions in the course of characteristic vibrations are clearly seen in the vibrational and vibronic spectra as absorption bands that retain their positions on the wave number scale (often, they also retain their intensities). This can be treated as the appearance of spectral indications of the RCs.

Summing up, a chemical transformation in a complex molecule is only possible if the atomic rearrangement occurs in a small spatial region, causes no significant changes in the geometric characteristics of the whole structure, and can occur in the case of a pure characteristic vibration or a combination of a small number of such vibrations. This can be determined with ease by monitoring animated pictures of atomic displacements from the equilibrium positions in the course of vibrations.[19,21–26] Quantitatively, the characteristic vibrations are indicated by the readily calculated shear vectors $b$ that describe structural deformations of the molecule upon chemical transformations in the system of normal coordinates.

Thus, we proposed a method of search for RCs in polyatomic molecules. Since displacement of a hydrogen atom requires the lowest energy and its migration is also accompanied by transfer of valence, reactions involving hydrogen atoms are typical of hydrocarbons and the rule

of conservation of the total valence holds for the synthesis or decomposition reactions by default.

Summing up, we revealed a number of specific features of the appearance of the RCs and of the processes occurring in them. The problem was treated *ab ovo* using no data obtained in chemical experiments, *i.e.*, only based on the basic principles of quantum theory. The results obtained in this work correlate with the available experimental data and provide a correct explanation for them.

This work was financially supported by the Council on Grants at the President of the Russian Federation (State Program for Support of Leading Scientific Schools in the Russian Federation, Grant NSh-5203.2006.3) and the Russian Foundation for Basic Research (Project Nos 04-03-32086a and 04-03-32087a).

## References

1. L. R. Khundkar, R. A. Markus, and A. H. Zewail, *J. Phys. Chem.*, 1983, **87**, 2473.
2. E. D. Potter, J. L. Herek, S. Pedersen, Q. Liu, and A. H. Zewail, *Nature*, 1992, **355**, 66.
3. J. S. Baskin, L. Baňares, S. Pedersen, and A. H. Zewail, *J. Phys. Chem.*, 1996, **100**, 11920.
4. *Femtochemistry: Ultrafast Chemical and Physical Processes in Molecular Systems*, Ed. M. Chergui, World Scientific, Singapore, 1996.
5. A. H. Zewail, *Adv. Chem. Phys.*, 1997, **101**, 892.
6. D. Zhong, E. W.-G. Diau, T. M. Bernhargt, S. De Feyter, J. D. Roberts, and A. H. Zewail, *Chem. Phys. Lett.*, 1998, **298**, 129.
7. A. N. Petrukhin, S. A. Antipin, F. E. Gostev, V. S. Marevtsev, A. A. Titov, D. G. Tovbin, V. A. Barachevskii, Yu. P. Strokach, and O. M. Sarkisov, *Khim. Fiz.* [*Chem. Phys.*], 2000, **19**, 90 (in Russian).
8. *The Reaction Path in Chemistry: Current Approaches and Perspectives*, Ed. D. Heidrich, Kluwer, Dordrecht, 1995.
9. M. E. Tuckerman, P. J. Ungar, T. von Rosenvinge, and M. I. Klein, *J. Phys. Chem.*, 1996, **100**, 12788.
10. D. Reichardt, V. Bonacic-Koutecky, P. Fantucci, and J. Jellinek, *Chem. Phys. Lett.*, 1997, **279**, 129.
11. G. Li and W. L. Hase, *J. Am. Chem. Soc.*, 1999, **121**, 7124.
12. T. Horii, Y. Abe, and R. Nakao, *J. Photochem. Photobiol. A*, 2001, **144**, 119.
13. Sh. Li, X. Yu, Zh. Xu, Z. Li, and Ch. Sun, *J. Mol. Struct. (THEOCHEM)*, 2001, **540**, 221.
14. R. M. Aminova and E. Ermakova, *Chem. Phys. Lett.*, 2002, **359**, 184.
15. V. I. Gol´danskii, L. I. Trakhtenberg, and V. I. Flerov, *Tunnel´nye Yavleniya v Khimicheskoi Fizike* [*Tunnelling Phenomena in Chemical Physics*], Nauka, Moscow, 1986, 293 pp. (in Russian).
16. R. P. Bell, *The Tunnel Effect in Chemistry*, Chapman and Hall, London, 1980.
17. S. Sato, *Chem. Phys.*, 2005, **315**, 65.
18. B. Jing, J.-Y. Liu, Z.-S. Li, Y. Wang, L. Wang, H.-Q. He, and C.-C. Sun, *J. Mol. Struct. (THEOCHEM)*, 2005, **732**, 225.
19. L. A. Gribov, *Ot teorii spektrov k teorii khimicheskikh prevrashchenii* [*From Theory of Spectra to Theory of Chemical Transformations*], Editorial URSS, Moscow, 2001, 365 pp. (in Russian).
20. B. I. Stepanov, *Vestn. Akad. Nauk Belorusskoi SSR* [*Bull. Acad. Sci. Belorussian SSR*], 1972, **3**, 67 (in Russian).
21. L. A. Gribov, *Zh. Fiz. Khim.*, 2001, **75**, 83 [*Russ. J. Phys. Chem.*, 2001, **75** (Engl. Transl.)].
22. L. A. Gribov, *Zh. Fiz. Khim.*, 2001, **75**, 290 [*Russ. J. Phys. Chem.*, 2001, **75** (Engl. Transl.)].
23. L. A. Gribov, *Zh. Fiz. Khim.*, 2001, **75**, 573 [*Russ. J. Phys. Chem.*, 2001, **75** (Engl. Transl.)].
24. L. A. Gribov, *Zh. Fiz. Khim.*, 2001, **75**, 1403 [*Russ. J. Phys. Chem.*, 2001, **75** (Engl. Transl.)].
25. L. A. Gribov, *Zh. Fiz. Khim.*, 2001, **75**, 1638 [*Russ. J. Phys. Chem.*, 2001, **75** (Engl. Transl.)].
26. L. A. Gribov, *Zh. Fiz. Khim.*, 2001, **75**, 1775 [*Russ. J. Phys. Chem.*, 2001, **75** (Engl. Transl.)].
27. V. I. Baranov and L. A. Gribov, *Izv. Akad. Nauk, Ser. Khim.*, 2003, 763 [*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 802 (Engl. Transl.)].
28. V. I. Baranov, M. V. Zavalii, and L. A. Gribov, *Zh. Prikl. Spektrosk.*, 2003, **70**, 628 [*Russ. J. Appl. Spectr.*, 2003, **70** (Engl. Transl.)].
29. V. I. Baranov and L. A. Gribov, *Zh. Prikl. Spektrosk.*, 2003, **70**, 735 [*Russ. J. Appl. Spectr.*, 2003, **70** (Engl. Transl.)].
30. V. I. Baranov and L. A. Gribov, *Zh. Fiz. Khim.*, 2004, **78**, 2180 [*Russ. J. Phys. Chem.*, 2004, **78** (Engl. Transl.)].
31. V. I. Baranov and L. A. Gribov, *Zh. Prikl. Spektrosk.*, 2004, **71**, 421 [*Russ. J. Appl. Spectr.*, 2004, **71** (Engl. Transl.)].
32. V. I. Baranov, M. V. Zavalii, and L. A. Gribov, *Zh. Prikl. Spektrosk.*, 2004, **71**, 295 [*Russ. J. Appl. Spectr.*, 2004, **71** (Engl. Transl.)].
33. V. I. Baranov and L. A. Gribov, *Zh. Fiz. Khim.*, 2005, **79**, 1265 [*Russ. J. Phys. Chem.*, 2005, **79** (Engl. Transl.)].
34. L. A. Gribov, V. I. Baranov, and M. V. Zavalii, *Russ. J. Phys. Chem.*, 2005, **79**, S154.
35. M. J. S. Dewar and R. C. Dougherty, *The PMO Theory of Organic Chemistry*, Plenum Press, New York, 1975.
36. 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 Computational Methods*], Nauka, Moscow, 1997, 475 pp. (in Russian).
37. L. A. Gribov, *Dokl. Akad. Nauk SSSR*, 1987, **292**, 1161 [*Dokl. Chem.*, 1987 (Engl. Transl.)].
38. L. A. Gribov and N. I. Prokof´eva, *Zh. Prikl. Spektrosk.*, 1987, **46**, 603 [*J. Appl. Spectr. USSR*, 1987, **46** (Engl. Transl.)].
39. M. V. Vol´kenshtein, L. A. Gribov, M. A. El´yashevich, and B. I. Stepanov, *Kolebaniya Molekul* [*The Vibrations of Molecules*], Nauka, Moscow, 1972, 700 pp. (in Russian).
40. L. A. Gribov, *Dokl. Akad. Nauk*, 2005, **404**, 54 [*Dokl. Chem.*, 2005 (Engl. Transl.)].

*Received May 23, 2005;*
*in revised form July 25, 2006*