

Molecular Dynamics of Stilbene Molecule under Laser Excitation

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1. INTRODUCTION

A detailed analysis of photo-stimulated structural transitions plays an important role in studying of organic molecules. This problem can be successfully solved by using optical methods since both linear and non-linear properties of organic molecules strongly depend on their structure.¹ Recent progress in the field of short laser pulse generation in pico- and femtosecond range² makes it possible to obtain detailed information on the structural dynamics of macromolecules.³ The computer molecular dynamics (MD) simulation method⁴⁻⁷ enables one to interpret the experimental information available and in many cases, to deepen and broaden understanding of the physics of processes taking place in molecules.

We report here on the MD study of the structure dynamics of a stilbene molecule excited by a laser pulse.⁸ Note, that the molecule of stilbene which was studied experimentally in detail^{3, 10-13} is of particular interest being a simple model for studying the mechanism of laser-induced molecular photoisomerization.

2. FORMULATION OF THE MD EXPERIMENT

The energetic parameters of various possible conformations of macromolecules can be studied using molecular mechanics calculations. The latter are based upon molecular energy dependence on the structure of molecules.¹⁴ By minimizing the potential energy of the molecule as a function of coordinates of its atoms one can determine both possible conformers (in potential energy local minima) and transition states (the saddle points). These methods are well developed and are widely used.¹⁵

At the same time, molecular structure dynamics, both in ground and excited electronic states, and the processes of electronic excitation have not yet been studied in detail. An approach to this problem was made by Birge *et al.*⁵⁻⁷ who have used semi-classical MD simulation to study conformational transitions in rhodopsin and bacteriorhodopsin. The isomerization reaction quantum yield and molecular trajectories of (including that in the presence of a solvent) motion have been calculated in those works. However, the development of the photo-isomerization reaction has been considered by the authors only in a direction along the corresponding torsion angle. In so doing, the processes of the internal energy redistribution in molecules have not been taken into account.

The same semiclassical MD method was used in the present work for studying the structural dynamics of the stilbene molecule (Fig. 1) excited by laser pulse. In so doing, consideration of all contributions to molecular potential energy $U(\mathbf{r}_1, \dots, \mathbf{r}_N)$ (energy of chemical bonds, valence and torsion angles, Van-der-Waals interactions, except electrostatic forces) enabled us to get detailed information on internal energy redistribution in a molecule and the dynamics of the structure of the latter.

Isolated molecule without any influence from the molecules of solvent was considered in order to make the model simpler. Experimentally this condition can be fulfilled for stilbene molecules in a supersonic molecular jet (see Ref. 10). The electronic excitation was assumed to be instantaneous and was defined by initial conditions imposed on stilbene geometry¹.

¹The detailed quantum theory of the single photon excitation of an electronic transition in multi-atomic molecule with subsequent calculation of dynamics of the molecule in excited state in phase space using the MD method can be found in Ref. 16.

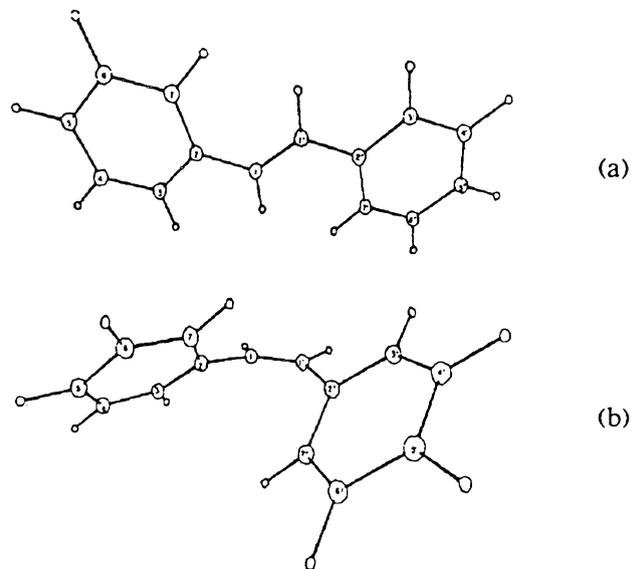


Fig. 1. Ground state equilibrium geometries of stilbene: (a) — trans-stilbene, (b) — cis-stilbene.

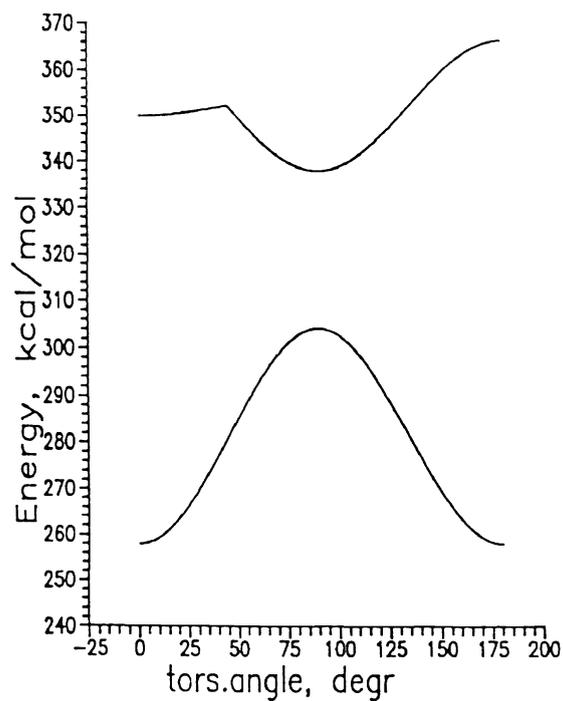


Fig. 2. Potential energy surfaces for the ground and excited electronic states as a function of the torsional angle (ethylene coordinate).¹³

Trajectories of motion for all atoms were obtained by numerical solution of classical Newton's equations:

$$m_i(d^2\mathbf{r}_i/dt^2) = -(\partial U/\partial\mathbf{r}_i) \quad i = 1, \dots, N, \quad (1)$$

where m_i and \mathbf{r}_i represent the mass and the position of the i -th atom, correspondingly.

The initial condition ($\mathbf{R}_0 = \{\mathbf{r}_1, \dots, \mathbf{r}_N\}$, $\mathbf{V}_0 = \{\mathbf{v}_1, \dots, \mathbf{v}_N\}$) was defined by coordinates found using special procedure of the potential energy surface minimization, by the temperature of the system and by type and the degree of electronic-vibrational excitation of the molecule. The found solutions $\mathbf{R}(t)$, $\mathbf{V}(t)$ provide information on the dynamics of the molecular structure and on the intra-molecular excitation energy redistribution.

2.1. Force field

The force $F_i = -\partial U(\mathbf{r}_1, \dots, \mathbf{r}_N)/\partial\mathbf{r}_i$, applied to the i -th atom of the molecule is completely determined by the potential energy of the latter

$$U(\mathbf{r}_1, \dots, \mathbf{r}_N) = U(q_1, \dots, q_{3N}) = U_b + U_{\text{val}} + U_{\text{tor}} + U_{\text{nb}}, \quad (2)$$

where U_b , U_{val} , U_{tor} , U_{nb} are the contributions due to deformations of chemical bonds, deviations of valence and torsional (dihedral) angles and Van-der-Waals interactions, respectively.

The choice of dependencies of these contributions on coordinates should be in agreement with the electronic structure of the molecule. Thus, the potential parameters are taken from experimental data, for example, from the x-ray structure analysis (the equilibrium values of coordinates $\mathbf{R}_0 = \{\mathbf{r}_1^0, \dots, \mathbf{r}_N^0\}$) and from vibrational spectroscopy ($\partial^2 U/\partial q_i \partial q_j |_{\mathbf{R}}$). All further analysis is made assuming that separate items in (2) in the ground and excited states differ only by the values of parameters.

Harmonic approximation¹⁷ was used for the bonds deformation and valence angles potentials

$$U_b = 0.5 \sum_b k_b (r - b_0)^2, \quad (3)$$

$$U_{\text{val}} = 0.5 \sum_\varphi k_\varphi (\varphi - \varphi_0)^2. \quad (4)$$

Here k_φ are the force constants of deformation, and φ_0 are equilibrium values of valence angles, correspondingly. The summation is made over all bonds and all equilibrium angles. The homogeneous length b_0 and force constant k_b are given for each bond (i, j); $r = |\mathbf{r}_i - \mathbf{r}_j|$ is the current length of the bond.

The Van-der-Waals (nonbonded) interactions are calculated for all couples of atoms (i, j), which do not belong to the same chemical bond, or for one and the same valence angle. The 6-exp function¹⁷ was used as a potential function

$$U_{\text{nb}} = f[2.25/rr^6 + 8.28 \times 10^5 \exp(-rr/0.0736)], \quad (5)$$

where $rr = r/s$, s is the sum of Van-der-Waals radii, f and s are determined by the kinds of atoms i and j .

The following approximation was used for the torsion angle potential:¹⁷

$$U_{\text{tor}} = 0.5 \sum_\theta k_\theta [1 + \cos(n\theta + \delta)]. \quad (6)$$

The force constant k_θ , the multiplicity of the potential surface and the phase shift δ were defined for each type of bonds.

The expression (6) was used for the description of the ground electronic state of stilbene. However, it was noted in Refs. 9, 18 that it is more preferable to use the potential surface instead of force constants for the excited state description in the case of molecules with delocalized π -electrons. Thus, the potential energy surfaces obtained by Syage *et al.*¹⁰ were used for the first excited state (Fig. 2).

The values of all parameters in (3)–(6) for stilbene molecule were taken from Ref. 17 and are given in Tables 1–4.

2.2. MD-trajectories and quantum yield of the photoisomerization reaction in stilbene

Semiclassical approach was applied for calculation of the MD-trajectories of isomerization, using dense levels approximation^{5,6}

$$(\Delta E_{\text{vib}}/\Delta t)_{t=\tau} = -|\Delta E_{\text{vib}}/\Delta t|_{\text{av}} \{1 - \exp[-\rho(E_{\text{vib}}(\tau) - kT)]\}, \quad (7)$$

where $(\Delta E_{\text{vib}}/\Delta t)_{t=\tau}$ is the rate of vibrational relaxation at trajectory time τ , $|\Delta E_{\text{vib}}/\Delta t|_{\text{av}}$ is the absolute (exponential) average vibrational relaxation rate, ρ is the density of states factor, $E_{\text{vib}}(\tau)$ is the vibrational energy at trajectory time τ , k is the Boltzman constant, T is the temperature.

The theoretical estimae of the quantum yield and the time of isomerization can be obtained from calculation of the transition probability to the ground state $a_0^2(\tau)$ along the MD-trajectory. The following $a_0^2(\tau)$ dependence along trajectory⁶ is used in semiclassical approximation:

$$a_0^2(\tau) = \exp \left\{ - \left([4\Delta E_{10}(\tau)/3h] [2\Delta E_{10}(\tau)/(\partial^2 \Delta E_{10}/\partial^2 t^2)_{t=\tau}]^{1/2} \right) \right\}, \quad (8)$$

where $\Delta E_{10}(\tau)$ is the adiabatic potential energy difference between the ground and excited state.

3. MOLECULAR DYNAMICS OF CIS-TRANS PHOTOISOMERIZATION IN STILBENE

The character and the degree of electronic-vibrational excitation of a stilbene by a laser pulse were given by various initial conditions in (1) in our MD-simulations. In so doing, we took into account the results of the stilbene vibrational spectrum analysis^{9,10} in the ground (S_0) and excited (S_1) electronic states. The main modes of the stilbene spectrum related to our analysis are given in Table 5.

The system of equations (1) was solved by using the Runge–Kutta method of the 4-th order with variable steps. The potential gradients were calculated analytically. Mean square deviations from the equilibrium values of bond length, valence and torsion angles were calculated every 40 fs and normalized by the corresponding equilibrium parameters.

3.1. Intramolecular energy redistribution

This series of experiments consists in investigation of the time scale of initial vibrational excitation energy redistribution. It is seen from Table 5 that low frequency out-of-plane modes are effectively excited in stilbene molecule as a result of interaction with a laser pulse. The results of computer experiments on combination modes excitation of the $C_e C_{e\text{stretch}}$ and CC_{stretch} bonds, in-plane modes and low frequency out-of-plane modes are shown in Figs. 3–10.

Analyzing the results of these experiments one can reconstruct the following sequence of events. During the first 800 fs the phenil rings excitation is redistributed into bending modes, torsion vibrations and stretching vibrations of the C–H bonds (Figs. 6, 9). After 1 ps weak energy exchange takes place between all modes with a characteristic time of ~ 2 ps. Torsion vibrations are excited immediately after laser excitation and are subsequently amplified, so that the torsion angle takes the value close to 90° after about 2 ps (Fig. 10).

Table 1. Interaction parameters for chemical bond potential.

Atom ₁	Atom ₂	b_0	k_b
C φ	C φ	1.395	700.0
C _e	C _e	1.520	316.8
C _e	C φ	1.525	320.0
C φ	H	1.084	346.0
C _e	H	1.100	331.2

Table 2. Interaction parameters for valence angles potentials (measurements units: φ_0 in degrees, $k\varphi$ in kcal mol⁻¹ degree⁻²).

Atom ₁	Atom ₂	Atom ₃	φ_0	$k\varphi$
C φ	C φ	C φ	120.0	0.012
C _e	C _e	C φ	120.0	0.013

Table 5. The most prominent vibrational modes in the excited state of *t*-stilbene¹³.

Mode	Frequency, cm ⁻¹	Relative intensity
C _e - Φ _{bend} (out-of-plane)	83.2	25
C _e - Φ _{torsion}	95.1	26
symmetrical ethylene bend	197.6	79
C _e - Φ (out-of-plane)	229	6.1
C _e CC _{bend}	280.3	30
C _e C _e - Φ _{bend} +CCC _{bend}	845.8—851.9	18
C _e - Φ _{stretch}	1250	10.6
CC _{stretch}	1548.4	3.5
C _e C _e stretch	1637.8	2.3

Table 6. Stastical analysis of the quantum yield of isomerization in stilbene after combination modes excitation.

τ ps	$a\delta^2(t)$	S ₁ %	S δ^{trans} %	S δ^{cis} %	τ_0 ps
2.68	0.005	99.5	0	0.5	—
2.76	0.15	84.6	14.9	25	—
2.89	0.31	41.5	33.5	25	4.10
3.22	0.53	19.5	33.5	47	4.10
3.55	0.34	12.9	40.1	47	4.72
3.66	0.61	5	40.1	54.9	—
3.68	0.64	2.8	43.2	54.9	—

Table 3. Interaction parameters for torsion angles potentials (measurements units: δ in degrees, $k\theta$ in kcal/mol).

Atom ₁	Atom ₂	Atom ₃	Atom ₄	$k\theta$	n	δ
any	C _e	C _e	any	6.0	-2	180

Table 4. Parameters of nonbonded interactions.

Atom	H	C
R _{VdV}	1.20	1.70
H	f_{HH}	f_{HC}
C		f_{CC}

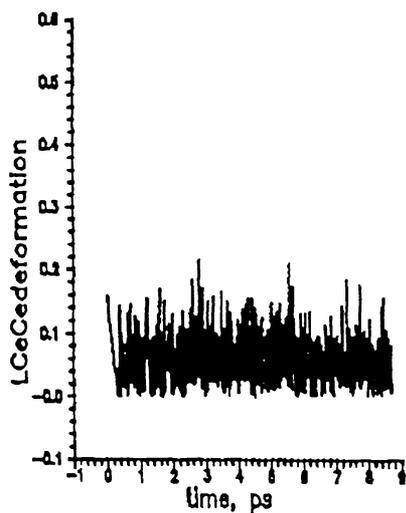


Fig. 3. Stretch dependence of $C_e - C_e$ bond of time during MD-experiment under the excitation of $C_e = C_e$ (combination modes excitation).

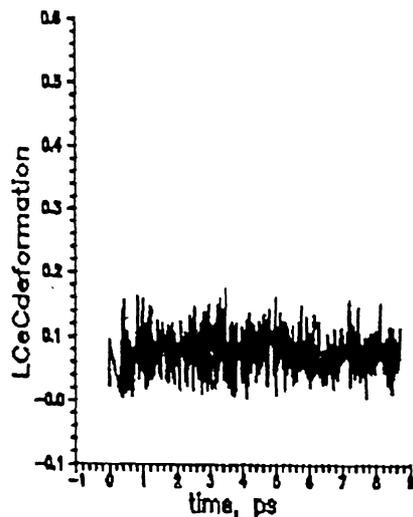


Fig. 4. Stretch dependence of $C_e - C_e$ bond of time during MD-experiment under the excitation of $C_e = C_\varphi$ (combination modes excitation).

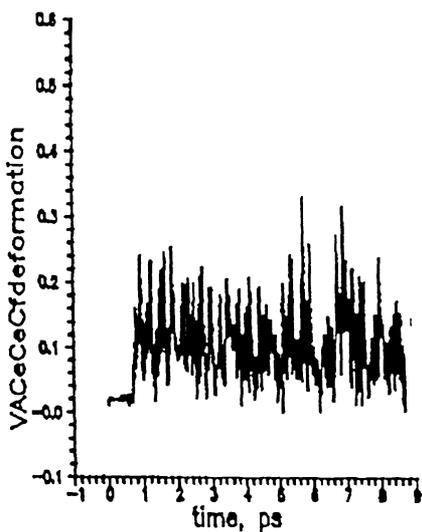


Fig. 5. $C_e - C_e - C_\varphi$ valence angle deformation dependence of time during MD-experiment under the excitation of $C_e - C_e - C_\varphi$ bend (combination modes excitation).

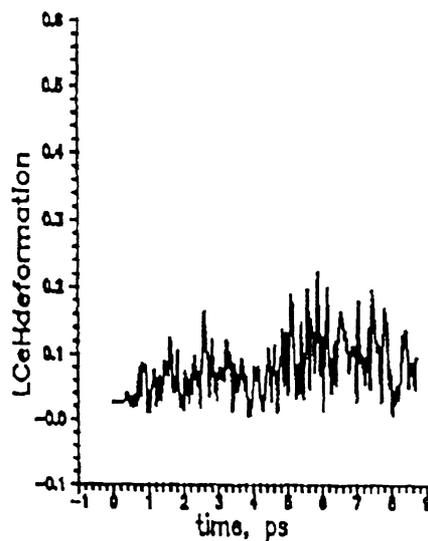


Fig. 6. Stretch dependence of $C_e - H$ bond of time during MD-experiment under the excitation of $C_e - H$ bend (combination modes excitation).

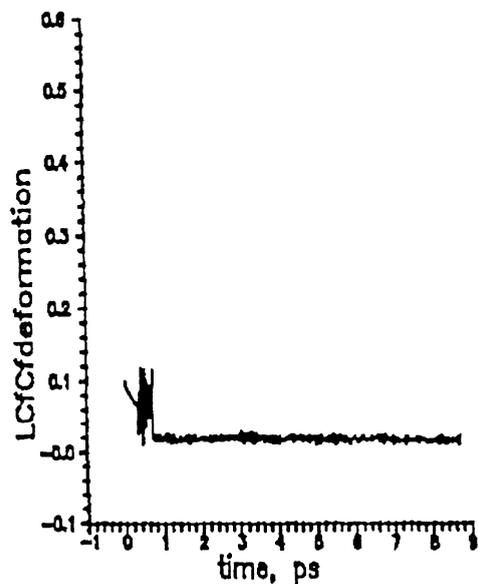


Fig. 7. Stretch dependence of $C_\varphi - C_\varphi$ bond of time during MD-experiment under the excitation of $C_\varphi - C_\varphi$ bend (combination modes excitation).

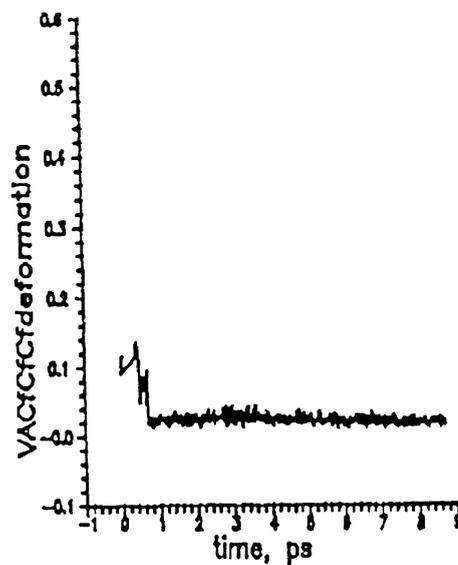


Fig. 8. $C_\varphi - C_\varphi - C_\varphi$ valence angle deformation dependence of time during MD-experiment under the excitation of $C_\varphi - C_\varphi - C_\varphi$ bend (combination modes excitation).

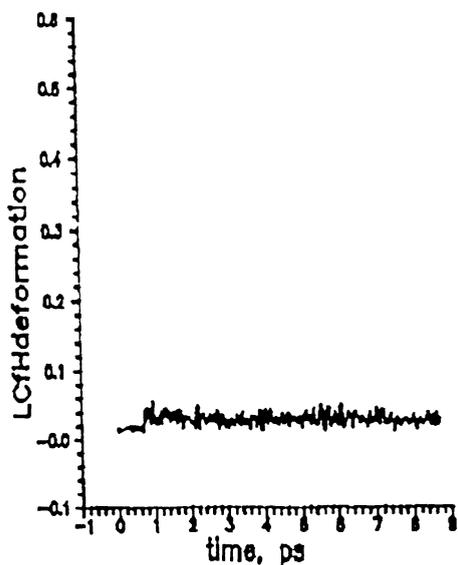


Fig. 9. Stretch dependence of $C_\varphi - H$ bond of time during MD-experiment under the excitation of $C_\varphi - H$ (combination modes excitation).

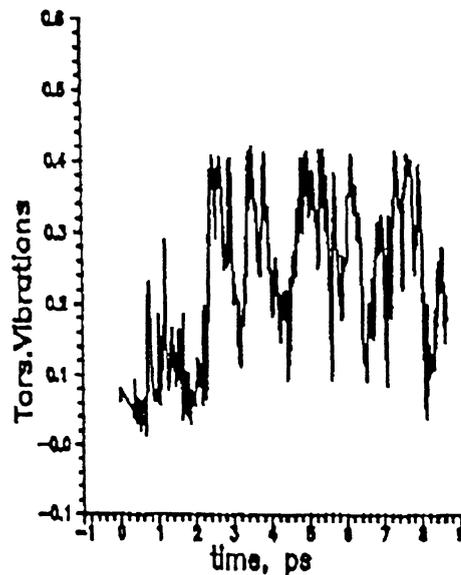


Fig. 10. Time dependence of amplitude of torsion vibrations during MD-experiment (combination modes excitation).

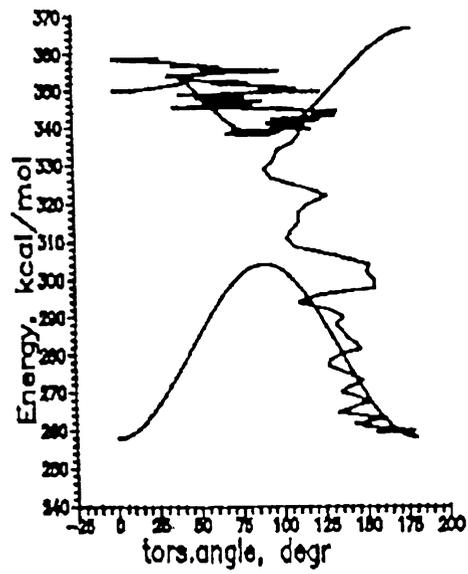


Fig. 11. Trajectory of molecular dynamics of trans-isomerization in stilbene.

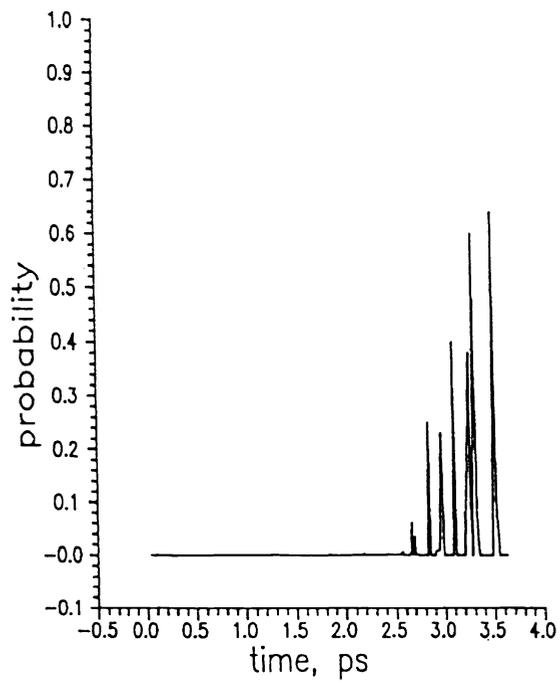


Fig. 12. Time dependence of stilbene isomerization probability during MD-experiment (combination mode excitation).

3.2. Photoisomerization

This next series of experiments consisted in studying of isomerization. The following values of the parameters were substituted in (7): $|\Delta E_{\text{vib}}/\Delta t|_{\text{av}} = 4 \text{ eV/ps}$, $T = 10^\circ \text{ K}$, $\rho = \exp(0.0042E_v)$ (see Ref. 13; E_v , cm^{-1}). Taking various values of the excitation energy in the range of 3.3–10 kcal/mole we observed the reduction of the isomerization time (by $\sim 200 \text{ fs}$ under strong excitation (6–10 kcal/mole). The typical results of the MD experiment are shown in Figs. 11, 12 (the excess energy in excited electronic state was $E_v = 8.2 \text{ kcal/mole}$).

The analysis of some photoisomerization trajectories is given in Table 6. The corresponding time dependence of the transition probability to the ground state is given in Fig. 12. The isomerization time is determined as a time interval necessary for the transition of more than $(1 - e^{-1})$ molecules from excited to ground state. The measured isomerization time is equal to 2.4 ps.

Besides calculation of the isomerization trajectories, the isomerization reaction quantum yield was also calculated using the following procedure. The first maximum of the transition probability to the ground state appears at 2.68 ps (Table 6), when 0.5% of molecules transfer to the ground state. The remaining 99.5% of molecules continue to move along the trajectories in excited state. The second maximum takes place at 2.76 ps, when the transition probability is about 0.15. Consequently, 15% of remaining molecules transfer from excited to ground state. After seven such maxima more than 98.1% of excited molecules are transferred to the ground state. As a result of it one obtains $\approx 54.9\%$ of cis-stilben molecules and $\approx 43.2\%$ of trans-stilben molecules.

4. DISCUSSION AND CONCLUSION

The results obtained in this work are in good agreement with experimental results of Ref. 3 except the estimate of isomerization time which has large values in the case of supersonic jet. The reason of this discrepancy might be the overstated value of the parameter $|\Delta E_{\text{vib}}/\Delta t|_{\text{av}}$ in (7).

In conclusion, we would like to stress that processes of intramolecular energy redistribution under laser excitation and the corresponding time scale were studied in this work by using MD method for the first time. Besides, isomerization trajectories, time and isomerization reaction quantum yield were calculated.

We believe, that further development of the MD approach to analysis of the processes of molecular excitation and intramolecular energy redistribution must be connected with the development of theory taking into account the quantum nature of excitation. In this case the creation of the corresponding distribution in the excited state by a laser pulse must be taken into account. The dynamics of this distribution in phase space can be analyzed by usual MD technique (see Ref. 16).

5. ACKNOWLEDGEMENTS

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