

## MD Investigations of Photoinduced Transformations in Organic Molecules

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### 1. ABSTRACT

A computer simulation procedure is developed for modeling intramolecular dynamics in polyatomic molecules. Electronic-vibrational excitation by ultrashort laser pulses (20 fs  $\div$  1 ps) is treated explicitly using quantum theory in harmonic approximation. MD simulation is used for studying the excited state dynamics. Stilbene photoinduced isomerization is modeled. Model potential energy surfaces (PES) for the ground and first excited singlet states are obtained using experimental absorption spectra in supersonic jet. Using a symmetrical along the torsional coordinate PES, it is shown that *cis*-stilbene undergoes the first stage of the isomerization reaction, i. e. transition to the twisted configuration, much faster than *trans*-stilbene, only due to the specific conformational properties.

### 2. INTRODUCTION

Many important processes in polyatomic molecules take place in excited electronic states or use them as transition states. Between these are photoinduced isomerization of retinal systems and photosynthetic bacteria, electron transfer in biological, interfacial, or electrochemical systems, vibrational relaxation in liquids, and photodissociation. These processes occur typically on pico- and subpicosecond timescales, and recent advances in generation of ultrashort and broadly tunable laser pulses are highly promising for experimental studies of the basic mechanisms realized in Nature.<sup>1-4</sup> Such investigations are important also in the search of new materials for nonlinear optics, electro-optics and molecular electronics.

The complexity of the objects under consideration, however, makes difficult a direct interpretation of the data obtained from different laser spectroscopy methods in both time and frequency domains. Thus, appropriate approximations and computer simulation methods are necessary.

Molecular Dynamics (MD) is a computer-based technique for modeling gases, liquids and solids on microscopic scales of distance and time, and is therefore an ideal technique for studying molecular behavior in many physical processes.<sup>5-7</sup> The method is based on the assumption that atomic motions are governed by classical mechanics provided some appropriate multidimensional force-field is used. Limitations of the method are well known. A fundamental one results from the basic assumptions of the method, namely, quantum-mechanical behavior is neglected and a single potential energy surface is assumed to govern the motion. The quantum nature of vibrational and electronic motion, however, is important and must generally be accounted for. Other problems are connected with practical difficulties in constructing accurate force-field, including large number of atoms, integrating over long times, or achieving accurate statistical sampling. All of these depend on the efficiency of the computational procedure and models used.

A general formulation of the problem and the approach used can be understood from Figure 1. A molecule being initially in a ground electronic state |1) after irradiation is excited to an upper electronic level |2). The initial state of the molecule after excitation depends on the two potential energy surfaces (PES) and laser pulse characteristics such as laser frequency, time duration and coherence length. The laser pulse duration  $\tau_p$  should be compared with the vibrational period  $\tau_v$  of the molecule. For instance, ultrashort laser pulse,  $\tau_p \ll \tau_v$ , would bring the molecule to the excited electronic state without sufficient changes in the nuclei configuration (Franck-Condon transition). In the quasi-stationary case a long laser pulse with sufficient coherence length would excite (under appropriate conditions) a single vibrational level (SVL). Actually a 15 ps laser pulse may be long enough for a SVL excitation.<sup>8</sup> In the intermediate case of comparable  $\tau_p$  and  $\tau_v$  the excited state is determined by a complex interference between vibrational movements in the two electronic states.

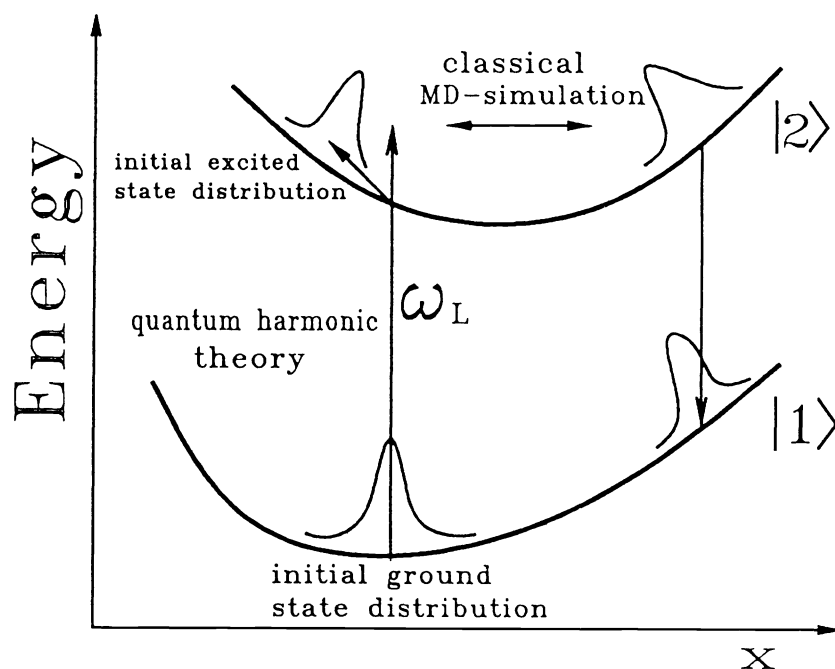


Figure 1. MD simulation of electronically excited polyatomic molecules. The excitation by ultrashort laser pulses is treated explicitly, using quantum harmonic theory. MD simulation is used for modeling the excited state dynamics.

Most often the experimental situation corresponds to the intermediate case with vibrational frequencies in the range of  $20\text{ cm}^{-1}$ – $3500\text{ cm}^{-1}$  and excitation by laser pulse in the range of  $20\text{ fs}$ – $1\text{ ps}$ . Elsewhere,<sup>9,10</sup> we have considered this intermediate case and presented a quantum harmonic theory of the one-photon electronic-vibrational excitation. The basic results of this previous study are as follows. The transition probability is given by

$$P(\omega_L) = (\Omega_L^2/4) \int f_p(\tau) \exp[i(\omega_L - \omega_{12})\tau] \chi(\tau) d\tau \quad (1)$$

where  $f_p(\tau) = \int u_p(s - \tau/2) u_p^*(s + \tau/2) ds$  is the laser pulse autocorrelation function,  $\Omega = E_L d_{12}/\hbar$  is the Rabi frequency,  $\omega_{12}$  is the frequency of the electronic transition;  $\chi(\tau)$  is analytical function of the frequency matrices  $\omega_1$  and  $\omega_2$ , the deviations  $\Delta$  of the energy minima along each vibrational coordinate, and temperature (see Eqs. (5–6) in Ref. 10).

After averaging the displacements of nuclei coordinates over the laser pulse one obtains

$$x_q = x_2 + \int p(\tau) \Delta x(\tau) d\tau / P(\omega_L) \quad (2)$$

where  $x_q$  is a  $3N$ -dimensional vector of the averaged coordinates after excitation;  $x_2$  is  $3N$ -coordinate vector of the energy minima point of  $|2\rangle$ ,  $p(\tau)$  is the time density of transition probability  $dP(\omega_L)/d\tau$  (see Eq. (1)),  $\Delta x(\tau)$  is the displacement relative to  $x_2$  at the moment of time  $\tau$  (see Eqs. (7–8) in Ref. 10). For the average momenta we have  $p_q = 0$ .

The absorption (excitation) spectrum or  $0^0$  dispersed fluorescence spectrum ( $0^0$  denotes the vibrationless excited electronic state) are calculated using Eq. (1), in which the integration is carried over a time period larger than all vibrational periods. In Sec. 3 we use the available absorption spectrum of stilbene molecule obtained in supersonic jets for precise determination of characteristics of 12 active normal modes (we use only modes well identified in the experimental spectrum). In doing so the PES are determined in harmonic approximation which may be useful in applications such as ultrafast excitation or early stage dynamics.

In Sec. 4 the PES are determined in a more general way by Molecular Mechanics (MM) potential energy functions. The correspondent parameters are calculated so as to ensure good agreement between calculated and experimental spectra. In Sec. 5 MD simulation results on the excited state PES (in the full  $3N$ -dimensional coordinate space) are reported. Using Eq. (2), MD trajectories are calculated with initial conditions given by the centers of weight of the wave packet. The dynamical behavior of *trans*- and *cis*-stilbene are compared.

### 3. SPECTRA CALCULATION AND NORMAL MODES CHARACTERISTICS

In harmonic approximation the molecule is considered as a set of  $3N - 6$  independent harmonic oscillators or normal modes ( $N$  is the number of atoms). If one neglects anharmonicities and Dushinski rotation each vibrational degree of freedom can be described by its frequencies in the ground and excited state, and by the displacement  $\Delta$  between the minima of the two states. Actually, in the absorption spectrum only a small number of modes with sufficient values of  $\Delta$  appear with sufficient intensity and are usually called optically active modes.

Using Eq. (1), Eqs. (5-6) in Ref. 10 and the developed computer procedure we simulate *trans*-stilbene supersonic jet absorption spectrum using the characteristics of 12 optically active normal modes. Their frequencies in the ground and first excited singlet state are known from supersonic-jets experimental spectra (see Tables 2 and 3 in Ref. 11). The simulation consists in varying the displacements along each mode until the relevant calculated intensities agree well with the experimentally obtained ones. The final result is presented in Figure 2 and Table 1. The simulation is straightforward, not surprisingly as the normal modes are independent, and the precision of the calculated characteristics is mainly determined by the precision of the experimental spectrum. This is also due to the effectiveness of the computational procedure allowing for a large number of iterations. A spectrum calculation takes of about 4 min with spectral resolution of  $1 \text{ cm}^{-1}$  on a 33 MHz i486-based computer. This is  $3N - 6$  dimensional calculation ( $N = 26$ ), though for only 12 modes  $\Delta \neq 0$ . In a similar calculation Shan *et al* determined the characteristics of 17 anthracene modes,<sup>12</sup> using a more general but not so efficient computational procedure.

The obtained normal mode characteristics may be used for constructing the molecular Hamiltonian in applications where the harmonic approximation is valid, for instance in consideration of ultrashort pulsed laser excitation and early stage dynamics.

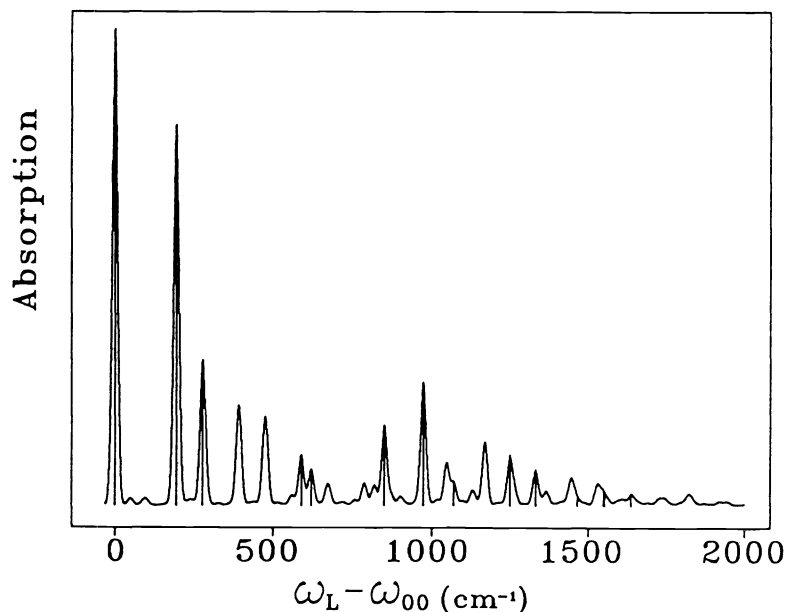


Figure 2. The absorption spectrum of jet-cooled *trans*-stilbene molecule calculated using 12 active modes (see Table 1). The calculation was made using Eq. (1) (see Eqs. (5-6) in Ref. 10)

Table 1. Vibrational frequencies and dimensionless displacements of 12 active modes of *trans*-stilbene.  $I$  is the calculated absorption intensity. The corresponding experimental values (see Table 2 in Ref. 11) are given in parentheses.

$\omega_0, \text{cm}^{-1}$	$\omega_1, \text{cm}^{-1}$	$\Delta$	$I, \text{a. u.}$
0	0		
204	197.6	1.21	78.5 (79)
290	280.3	0.75	30.0 (30)
624	590.7	0.32	10.0 (10)
870	850	0.56	16.9 (17)
1006	972.7	0.70	25.8 (26)
1072	1069.8	0.26	4.9 (5)
1031	1249.3	0.38	10.3 (10.6)
1340	1332.4	0.34	6.8 (7.5)
1495	1464	0.12	1.8 (1.7)
1584	1548.4	0.20	3.0 (3.5)
1607	1553	0.16	1.7 (1.9)
1654	1637.8	0.17	2.2 (2.3)

#### 4. USING OF MOLECULAR MECHANICS METHOD FOR CALCULATION OF THE GROUND AND EXCITED STATES' POTENTIAL ENERGY SURFACES

In many applications harmonic approximation is not adequate and a more general determination of the PES is necessary. As an example, in this section we determine the PES of the ground and the electronically excited states of stilbene molecule by means of the Molecular Mechanics (MM) potential energy functions. MM functions have been developed and parameterized on the basis of structural and thermodynamic experimental data. In this work, with the example of stilbene molecule, we parameterize our force field using the absorption spectrum obtained in supersonic jet experiments.<sup>11</sup>

We use the following MM potential energy functions:<sup>13</sup>

$$U(r_1, \dots, r_N) = U_b + U_{va} + U_{tor} + U_{vw} , \quad (3)$$

where  $U_b$ ,  $U_{va}$ , and  $U_{tor}$  are contributions due to deviations of chemical bonds lengths, valence and torsional (dihedral) angles from their equilibrium values, respectively,  $U_{vw}$  being the contribution due to Van-der-Waals interactions.

Deformations of chemical bonds lead to increase of the energy:

$$U_b = 0.5 \sum_b k_b (b - b_0)^2 , \quad (4)$$

where the sum is taken over all bonds. For every bond  $(i, j)$  its equilibrium length  $b_0$  and stretching force constant  $k_b$  are known;  $b = |\vec{r}_i - \vec{r}_j|$  is the current bond length.

The deviations of valence angles  $\varphi$  from their equilibrium values  $\varphi_0$  lead to the following increase in energy:

$$U_{va} = 0.5 \sum_{\varphi} k_{\varphi} (\varphi - \varphi_0)^2 , \quad (5)$$

where  $k_{\varphi}$  are the bending angle force constants, and the sum is taken over all valence angles.

The potentials of dihedral (torsional) angles  $\theta$  are taken in the following form:

$$U_{\text{tor}} = 0.5 \sum_{\theta} V_{\theta} [1 - \cos(n\theta)] \quad (6)$$

Here for every kind of torsional angles one has to set the values of force constant  $V_{\theta}$  and potential multiplicity  $n$ .

Van-der-Waals (nonbonded) interactions are calculated for all pairs of atoms ( $i, j$ ) which do not belong to the same chemical bond or the same valence angle:

$$U_{\text{vw}} = \sum f [-2.25/R^6 + 8.28 \times 10^5 \exp(-R/0.0736)] \quad (7)$$

where  $f$  is the force constant;  $R = r_{ij}/s$ ,  $s$  is sum of Van-der-Waals radii determined by the types of atoms  $i, j$ , and  $r_{ij} = |\vec{r}_i - \vec{r}_j|$ .

All the equilibrium bond lengths, valence angles and Van-der-Waals radii are well known<sup>13</sup> and may be used directly. The transferability of the force constants has been proved for a large number of molecules. For dynamic investigations, however, the force constants should be adjusted additionally, as well as the equilibrium bond lengths and valence angles of the excited molecule. Using the standard technique we calculate the frequency matrix of the ground state and vary the force constants of the MM PES (4-7) until a good fit to the available experimental data is obtained. As a result we can characterize entirely the ground PES and with the finally accepted parameters the calculated frequencies correspond to the experimental values (see Tables 1-3 in Ref. 11) with deviations less than  $10 \text{ cm}^{-1}$ .

For the excited state we accept the same potential energy functions as that for the ground state and look for the changes of the parameters accounting for the absorption and  $0^0$  dispersed fluorescence spectrum. Spectra are calculated using Eq. (1). The main features of the spectra are determined by the normal modes deviations of the two terms  $\Delta = (x_2 - x_1)$  and the differences of the frequency matrices  $\omega_1$  and  $\omega_2$  or, correspondingly, by the changes of the parameters of the MM PES. Spectra are most sensitive to changes in the equilibrium bond lengths. As a rule, bond lengths increase in an excited state. However, in stilbene, delocalization of the double bond results in stretching of the ethylene bond  $C_e=C_e$  and compression of  $C_e$ -phenyl bond in the excited state compared to their lengths in the ground state. In our calculations we also find out that changes in bond lengths larger than  $0.01 \text{ \AA}$  lead to highly congested unresolved spectra, while it is known from the experiment that the spectra consist of well-resolved lines. Consequently, we used an iterative procedure for calculating the parameters of the excited PES, varying their values in thus obtained limits.

The finally accepted parameters are given in Table 2 and the calculated spectrum is shown in Figure 3. It fits well the experimental data from Ref. 11, showing the same trends for the dominant peaks and a similar background.

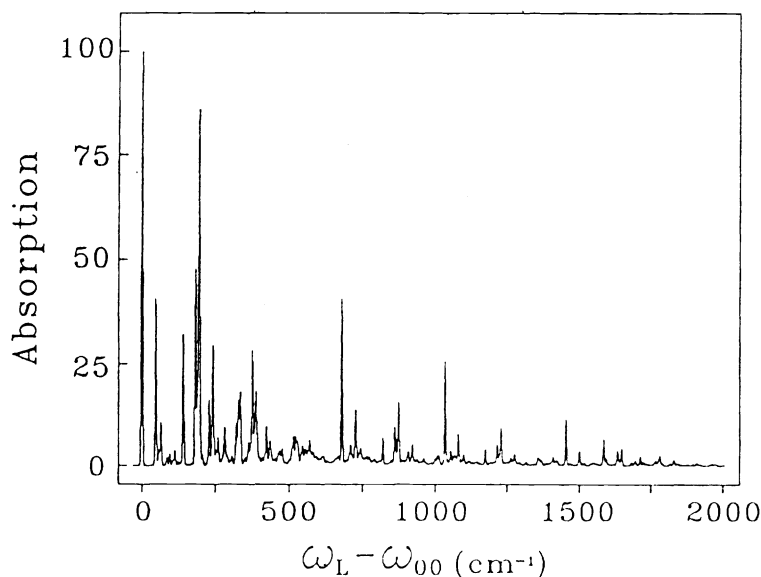


Figure 3. The calculated absorption spectrum of jet-cooled *trans*-stilbene. The calculation was made using Eq. (1) and potential energy surfaces determined by Molecular Mechanics method using Eqs. (4-7) and parameters given in Table 2;  $\omega_{00}$  is the vibrationless electronic transition frequency.

Table 2. Parameters of MM PES (see Eqs. (4-7)) used in calculation of the absorption spectrum presented in Figure 3.

Parameters for bond stretching potentials

Bond	Ground state		Excited state	
	$k_b$ (kcal/mol $\times\text{\AA}^2$ )	$b_0$ (\AA)	$k_b^*$ (kcal/mol $\times\text{\AA}^2$ )	$b_0^*$ (\AA)
$C_\phi - C_\phi$	993.7	1.397	893.0	1.397
$C_\phi - H$	725.6	1.113	725.0	1.113
$C_e = C_e$	1150.0	1.338	750.0	1.343
$C_\phi - C_e$	818.0	1.458	1100.0	1.451
$C - H$	725.6	1.113	720.0	1.114

Parameters for angle deformation potentials

Angle	Ground state		Excited state	
	$k_\varphi$ (kcal/mol $\times\text{deg}^2$ )	$\varphi_0$ (deg)	$k_\varphi^*$ (kcal/mol $\times\text{deg}^2$ )	$\varphi_0^*$ (deg)
$C_\phi - C_\phi - C_\phi$	0.0016	120	0.0013	120.1
$C_\phi - C_\phi - H$	0.0014	120	0.0011	120.4
$C_\phi - C_\phi - C_e$	0.0010	120	0.0008	121.3
$C_\phi - C_e - C_\phi$	0.0012	120	0.0010	120.0
$C_\phi - C_e - C_e$	0.0014	120	0.0008	121.7
$H - C_e - C_e$	0.0015	120	0.0009	120.8

Parameters for torsional potentials

Bond	Ground state		Excited state	
	$k_\theta$ (kcal/mol)	$n$	$k_\theta^*$ (kcal/mol)	$n^*$
$C_\phi - C_\phi$	3.0	-2	3.0	-2
$C_\phi - C_e$	3.0	-1	3.1	-2

Parameters for Van-der-Waals potentials

Atom(s)	$f$ (kcal/mol)	$R_{vdw}$ (\AA)
C-C	0.107	—
C-H	0.067	—
H-H	0.042	—
C	—	1.7
H	—	1.2

## 5. MD SIMULATIONS OF EXCITED STATE DYNAMICS

### 5.1. General scheme

A general scheme of the computer experiments which are possible with the developed simulation programs is presented in Figure 4. Using a standard MM program or self-made minimization procedure and the expression for the force field one obtains the equilibrium molecular structure. Then, as it has been described in Sect. 4, using Eq. (1) it is possible to calculate the force field parameters in accordance with the available experimental data. We note, however, that the computer simulation is not straightforward. The spectrum is determined by the characteristics of the normal modes (see Sect. 3) while in the simulation one varies the force field parameters. For a certain force field it may be not possible to obtain appropriate parameters.

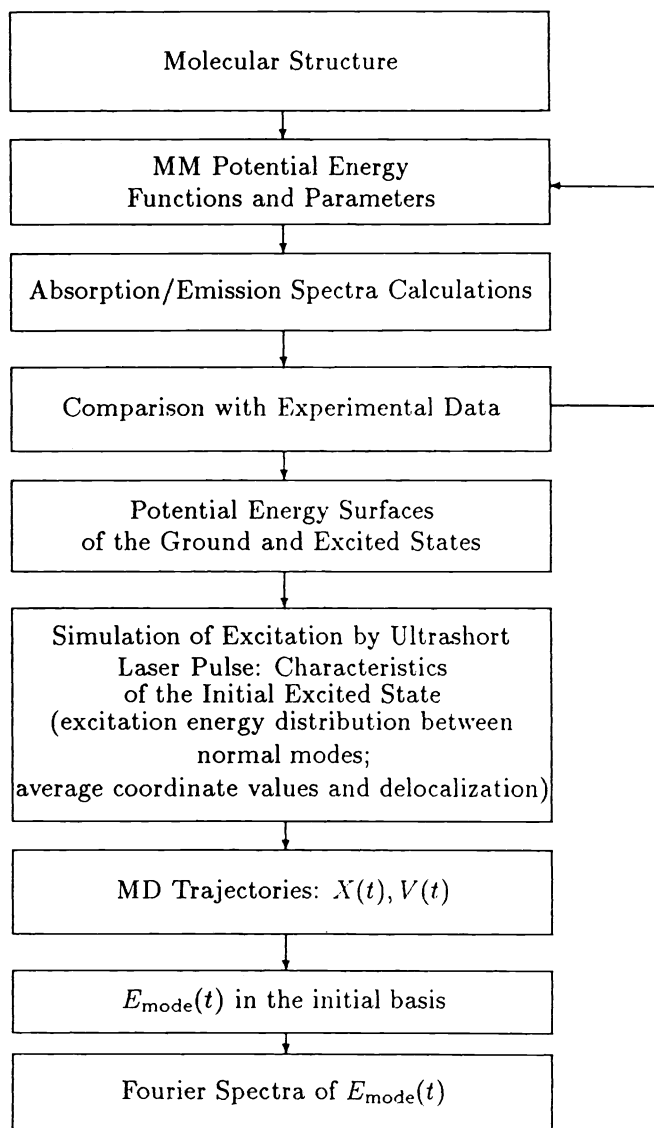


Figure 4. General scheme of computer experiments on photoinduced excited state dynamics.

Having determined the PES of the ground and excited states one uses the standard technique for obtaining the eigenvalues and vectors for the matrices of the potential energy second derivatives. The eigenvalues determine the frequency matrices, while the eigen vectors determine the basis for transformation of Cartesian coordinates

to normal coordinates. Using this initial basis and calculated MD trajectories it is possible to monitor the time evolution of the energy in all vibrational modes. The Fourier spectra of these time-dependencies reveal the typical frequencies of the energy exchange between the normal modes. For calculating MD trajectories in the excited state the initial coordinates should be determined by using the calculated average (over the excitation pulse duration) coordinates (Eq.(2)) and their delocalization  $\Delta x$  (Eq. (8) in Ref. 10).

We have used this procedure for modeling ultrashort pulsed laser excitation (a number of modes with sufficient  $\Delta$ -s excited simultaneously) or SVL excitation and study of the processes of intramolecular vibrational energy redistribution (IVR) in anthracene ( $C_{14}H_{10}$ ) and *p*-difluorobenzene ( $C_6F_2H_4$ ).<sup>14</sup>

## 5.2. MD study of the photoinduced stilbene isomerization

Stilbene (1,2-diphenylethylene) has been studied extensively as a model system for isomerization dynamics. The two conformers, *trans* and *cis*, are divided by a 46 kcal $\times$ mol<sup>-1</sup> potential barrier in the ground electronic state. In the first excited singlet state, however, only a small barrier of about 3.3 kcal $\times$ mol<sup>-1</sup> is known to exist (as found from supersonic jet experiments), not far away along the torsional coordinate. Ground state equilibrium geometries of the two conformers are shown in Figure 5, and the torsional dependences for the ground and excited states are shown in Figure 6. Typical isomerization times vary from  $\sim$  200 ps to  $\sim$  10 ps in vapors and different solvents, depending, also, on the excitation wavelength. The times of *cis*-stilbene isomerization are much less (of about 1  $\div$  2 ps) and using of a barrierless PES or very small barrier to isomerization is accepted.<sup>15-18</sup> The information deduced from experiments is, however, related to an effective PES, because after a certain amount of energy is transferred to the molecule, the latter undergoes the transition.

Here we will use the MM PES determined in Sec. 4. The torsional dependence (see Eq. (6)) along the  $C_6C_7C_8C_9$  torsional angle in this model would coincide with a quantum chemical calculation in which only this angle is varied, all other parameters being constant. Performing the calculation described in Sec. 4 we ensure that the harmonic part of our PES is in accordance with the experimental data. The anharmonic part of the potentials may be proved only by means of explicit dynamic calculations. We point out, however, that the anharmonic part of the potential is not determined only by Eqs. (6-7). Although, the other two potentials, Eqs. (4-5) are a harmonic approximation with respect to internal coordinates, they contribute to anharmonic terms due to the nonlinear relation between internal and normal coordinates. An estimation using 3-th and 4-th order derivation matrices shows a reasonable anharmonic part of the potentials. In previous studies<sup>19</sup> we found that in the isomerization reaction only small changes of the bond lengths (less than 5 %) and of the valence angles (less than 8 %) occur. Consequently, a reasonable model is to use the calculated parameters for the whole time of the reaction and to determine additionally only the energy dependence on the torsional coordinate. We used the following expression for ethylenic bond contribution in the excited PES (see Figure 6):

$$U_{\text{eth}} = V_1 \sin^2(2\theta) - V_2 \cos^2(\theta - \theta_0) , \quad (8)$$

where  $\theta$  is the torsional angle corresponding to twisting of the molecule around the double ethylenic bond, and  $\theta_0 = 90^\circ$ . Parameters  $V_1$  and  $V_2$  determine the local barrier of isomerization (region A in Figure 6) and the deeper potential well around the twisted geometry (region B in Figure 6). We use  $V_2 = 8$  kcal $\times$ mol<sup>-1</sup> and different values of  $V_1$  in this way modeling different values of the local barrier  $E_1$  and its position along the torsional coordinate  $\theta_1$  (see Figure 6b). This simple analytical function enables for modeling of a barrierless potential (with  $V_1 = 0$ ), a flat local potential (for instance, with  $V_1 = 2$  kcal $\times$ mol<sup>-1</sup> the potential is flat with accuracy of 0.001 kcal $\times$ mol<sup>-1</sup> over  $8^\circ$ , see Table 3), and with small local barrier (see Figure 6b and Table 3).

To perform a MD study of the excited state dynamics we simulate molecule excitation by ultrashort 40 fs laser pulse with frequency exceeding the frequency of the vibrationless transition by 3000 cm<sup>-1</sup>. Using Eq. (2) we calculated the coordinates averaged over the time of excitation and use them as a starting point for the MD trajectory. For integration of the equations of motion we use 4-th order Runge-Kutta algorithm with adaptive stepsize control ensuring conservation of the total energy within an accuracy of 2 %. Along the obtained MD-trajectories we calculate the torsional angle ( $C_6C_7C_8C_9$ ). Typical dependencies of the torsional angle on time are shown in Figure 7 for the two conformers. One and the same PES determined by Eqs. (3-8) was used, under one and the same excitation. Nevertheless, the dynamic behavior of the two conformers is different. The *cis*-stilbene molecule undergoes transition to the twisted conformation much faster than *trans*-stilbene. The results for different values of the local barrier and its position along the torsional coordinate are shown in Table 3 (all other parameters



of the PES retained values given in Table 2). Most likely, the different dynamic behavior is due to the strong Van-der-Waals interactions between atoms C<sub>6</sub>, C<sub>14</sub>, H<sub>15</sub>, and H<sub>21</sub> in *cis*-stilbene (see Figure 5).

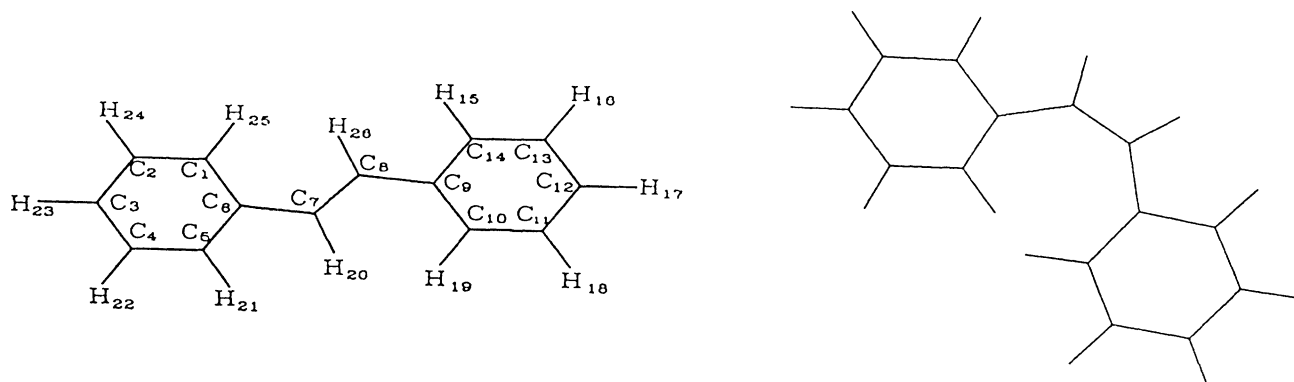


Figure 5. Ground state equilibrium geometries of *trans*- (left) and *cis*-stilbene (right).

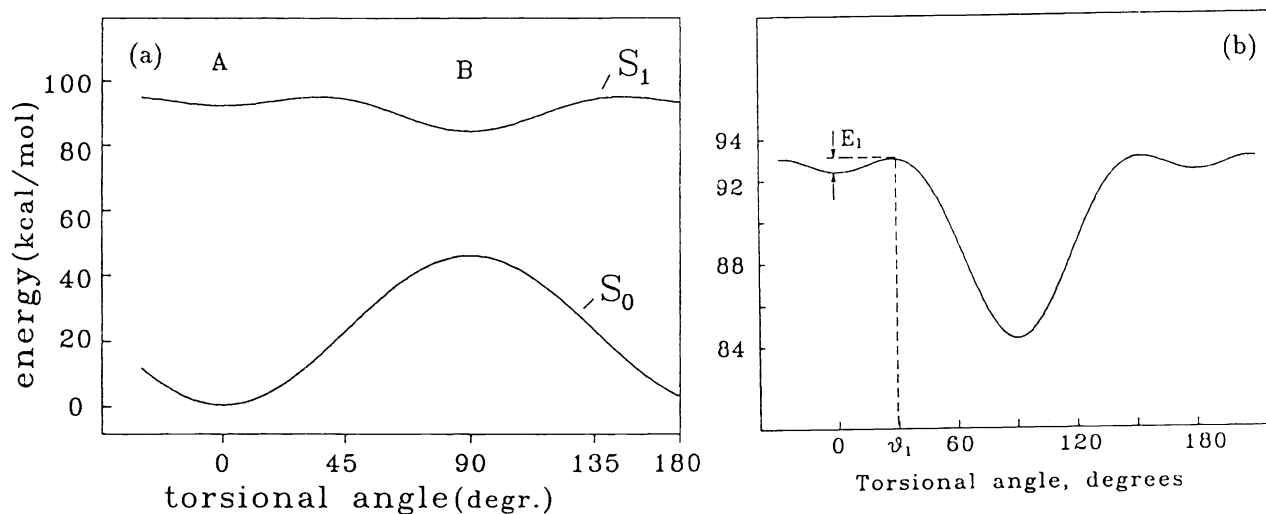


Figure 6. The potential energy surfaces for the ground and excited electronic states of stilbene as a function of ethylene torsional coordinate (a) and the torsional potential for the excited state (b, see Eq. (8)). The local barrier  $E_1$  and its position  $\theta_1$  along the torsional angle are determined by parameters  $V_1$  and  $V_2$  in Eq. (8).

## 6. CONCLUSION

Frequency- and time-resolved absorption/emission spectra recorded in supersonic jets contain a large amount of information about the potential energy surfaces of the ground and electronically excited states, and about the purely intramolecular photoinduced dynamics. Previously, using the first order perturbation theory for the quantum density matrix and local quadratic approximation of the PES near the ground state equilibrium coordinates we have found out exact expression for the one-photon quantum transition probability  $P(\omega)$ , giving its dependence on the frequency matrices and the normal modes' displacements of the both electronic terms (see Eq. (1)). If, then, one uses any appropriate way of determining the PES, spectra calculation based on these equations can be used for adjusting the parameters of the PES. Otherwise, if only experimental spectra are available, the frequency matrices are determined to some extent and the dimensionless normal modes displacements can be calculated in a computer simulation (Sec. 4). We determined the PES by means of the MM potential energy functions. They are relatively simple and widely used in structural studies of organic molecules. We have shown that the MM potential energy

functions can also be used successfully for dynamical studies and some of the parameters can be determined.

After the PES or equivalently (in harmonic approximation) the frequency matrices and the dimensionless displacements of normal modes are determined, some characteristics of the excited state can be calculated and used for an accurate MD or wave packet analysis of the molecule's dynamics after excitation. As a first guess, the coordinates  $x_q$  averaged over the pulse duration (see Eq. (2)) may be used as initial conditions for the equations of motion. For a more precise quantitative results, a statistical averaging of the delocalization  $\Delta x$  during the excitation should be done.

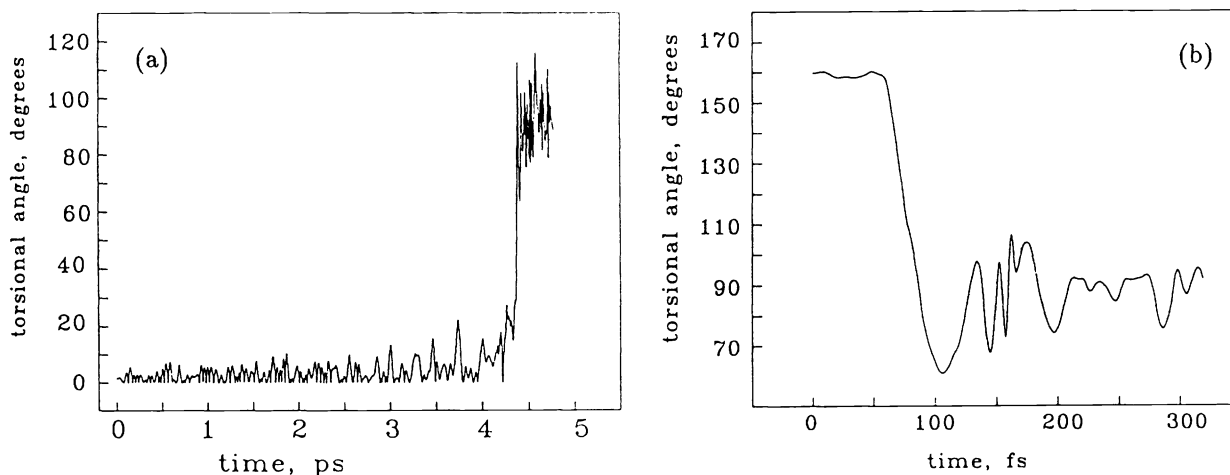


Figure 7. Typical dependences on time of the torsional angle  $C_6C_7C_8C_9$  (see Figure 5), calculated along MD trajectories for *trans*-stilbene (a) and *cis*-stilbene (b). The potential energy surfaces are determined by Eqs. (3–8) and Table 2. In Eq. (8)  $V_1 = 2.9 \text{ kcal}\times\text{mol}^{-1}$ ,  $V_2 = 8 \text{ kcal}\times\text{mol}^{-1}$ . The initial coordinates for MD trajectories are calculated using Eq. (2), simulating molecule excitation by 40 fs Gaussian laser pulse with excess vibrational energy  $E_v = 3000 \text{ cm}^{-1}$ .

Table 3. *Trans*- and *cis*-stilbene dynamics on the excited PES ( $3N$ -dimensional). The time for reaching the twisted conformation depends on the parameters of the ethylene torsional potential (see Eq. (8)). All other parameters, Eqs. (4–7), are kept as in Table 2.

Torsional potential parameters				stilbene	
$V_1$ (kcal/mol)	$V_2$ (kcal/mol)	$\psi_1$ (degr.)	$E_1$ (kcal/mol)	trans $\tau_{90}$ (fs)	cis $\tau_{90}$ (fs)
0	8	0.000	0.00	112	37
2	8	8.667	0.00	302	52
2.5	8	20.000	0.10	1087	65
2.8	8	23.333	0.23	3282	78
2.9	8	24.667	0.28	4221	86
3.1	8	26.00	0.39	6889	102
3.3	8	27.333	0.51	10554	189
3.5	8	28.667	0.64	15318	1889

We have presented a general scheme of the computer experiments, which can be made with the developed molecular simulation packages (see Sec. 5.1). Our results on the excited state dynamics of stilbene show that the different dynamic behavior of the *trans*- and *cis*-stilbene can be accounted for by the specific conformational interactions

rather than by an asymmetry of the PES along the torsional coordinate.

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