Ultrafast dynamics of surface-adsorbed conjugated molecules

S. Yu. Kotkov, V. N. Zadkov, B. A. Grishanin

Department of Physics, Moscow State University, Moscow 119899, Russia

V. D. Vachev and J. H. Frederick

Department of Chemistry, University of Nevada, Reno, Nevada 89557-0020

ABSTRACT

A detailed computer examination of the excited state dynamics of stilbene, both isolated in the gas phase and physisorbed on an inert surface is presented. It is discussed how the surface affects stilbene's dynamics in comparison with the isolated molecule case.

1. INTRODUCTION

In many cases, the design of photochromic materials, organic conductors, and nano-switches centers upon a fundamental understanding of conjugated π-systems and their physical properties and chemical transformations. The present paper is focused on a detailed examination of the excited state dynamics of conjugated molecules, both isolated in the gas phase and physisorbed on an inert surface. By obtaining a fundamental understanding of the dynamical processes such systems can undergo in both environments, we hope to gain insight into not only how desired isomerization channels might be enhanced and controlled, but also how a surface can influence a photoisomerization process.

The general strategy used in all of our investigations can be outlined as follows. First, an empirical Born-Oppenheimer Potential Energy Surface (PES) is constructed for the isolated molecular system of interest using a combination of spectroscopic fitting techniques, *ab initio* information about the molecular structure, and standard molecular modeling force fields. If necessary, surfaces for both the ground electronic state and one more excited electronic states are constructed. The interaction of the system with a radiation field is then simulated to determine the non-stationary state that is prepared by an ultrafast (i. e. femtosecond) laser pulse using a semiclassical algorithm developed previously.[1-3] Finally, the molecular dynamics of that non-stationary state is determined numerically using classical molecular dynamics algorithms.

As an extension of the approach we have successfully applied to the ultrafast dynamics of isolated photoexcited polyatomic molecules, we have also theoretically investigated optically driven nonthermal surface reactions. Here, we simulate a single molecule's dynamics on a surface, and focus on cases involving only "physical interactions" in the molecule–surface system, that is, when there is no chemisorption. In the case of stilbene, for example, we model the molecule-surface interaction using only van der Waals-type interactions. In this way, we can simply extend the molecular modeling empirical potential surfaces used previously by adding pairwise atom–atom interactions between the molecule and the atoms that constitute the surface.

In the presence of an applied intense laser field, there also exists induced-dipole–image-dipole interaction between the molecules and the substrate.[4] We treat these field-induced interactions as an "electromagnetic" interaction in the dynamics simulations. Again, because of the size of the system, extensions of our semiclassical expressions for ultrashort pulse excitation can be used to model this process and all dynamics can be simulated using the classical molecular dynamics method.

In this work we are only concerned with the regular van der Waals interactions as perturbations on the isolated molecule, and answers are given to the following questions: (i) How do adsorbed molecule's spectra compare to the spectra obtained in supersonic jet experiments? (ii) What are the differences in adsorbed molecule's dynamics (isomerization time, IVR rates, etc.) in comparison with the isolated molecule's dynamics?

To answer these questions, we considered a stilbene molecule on the surface of a graphite lattice. Neglecting collective interactions we represent the lattice potential as a sum of potentials due to individual C-atoms. To describe the molecule–lattice interaction we used the same force constants which were adopted earlier for stilbene Molecular Mechanics (MM) potential.[3] Here we restrict the graphite lattice model to a single surface layer, in order to minimize the calculation time. After that we have investigated what initial equilibrium configurations of a molecule relative to

the surface are possible. Next, for these equilibrium configurations we have calculated the absorption spectra of *trans*-stilbene on the surface and compared it with the one predicted for an isolated molecule within the same calculation scheme and the same MM parameters. Finally, we have performed a series of dynamics calculations and obtained dynamic trajectories both for an isolated and surface-adsorbed *cis*-stilbene molecule excited with a 100 fs Gaussian laser pulse with 4000 cm^{-1} excess vibrational energy.[3] Here we are interested just in the *cis-trans* isomerization channel and do not take into account the interaction responsible for *cis*-DHP isomerization.[3]

2. EQUILIBRIUM STATE OF STILBENE ON A GRAPHITE LATTICE

Due to the assumption that the molecule of interest has no chemical bonds with the surface, we can reasonably describe their interaction potential with the well-known formula for van der Waals (nonbonded) interactions. These are calculated for all pairs of atoms (i, j) using a Hill type potential[5] involving two parameters for each atom: one is the van der Waals' radius of the atom, and the other is an energy scale factor. The function representing the potential consists of attractive term varying as r^{-6}, which represents dipole/induced dipole interaction, and repulsive term which is exponential. A latent problem with this type of function is that at small atom distances the potential turns over and becomes strongly attractive. To prevent this from becoming a factor in the present study, especially in finding the equilibrium configuration of the molecule on the surface, an exponential repulsion term is fit to the potential function at the inflection point so that the potential and its first derivative are continuous

$$U_{vw} = \sum_r \begin{cases} f\left[-2.25/r_n^6 + 8.28 \times 10^5 \exp(-r_n/0.0736)\right], & \text{if } r \geq r_0; \\ V \exp(-kr_n), & \text{otherwise.} \end{cases} \tag{1}$$

Here f is proportional to the depth of the potential and depends on the identity of the two atoms; and $r_n = r_{ij}/s$, where s is sum of the van der Waals radii for atoms i and j, and $r_{ij} = |r_i - r_j|$. The total potential is

$$U_{tot} = U_{mol} + U_{int}, \tag{2}$$

where U_{mol} is just the MM potential of an isolated stilbene molecule including nonbonded interactions and U_{int} is a molecule–lattice interaction potential introduced for each pair of atoms belonging to the molecule and the surface respectively with the use of Eq. (1). Both for U_{mol} and U_{int} parameters we used the values obtained previously.[3] There are no additional parameters except the geometrical size of the layer's cell. We used the computer program of Ref. 2 modified by changing the potential to the total one introduced by Eq. (2) for the PES of a surface adsorbed molecule.

We begin our calculations with an investigation of the possible equilibrium states of the molecule on the lattice, with the molecule being in the ground electronic state. To obtain the equilibrium configurations we calculate dynamical trajectories in the lattice's potential and introduce velocity damping in the equations of motion. The initial conditions are chosen to correspond to the initial separation between a molecule and the surface ≥ 5 Å. The molecule's potential energy depends most strongly on the orientation angle of the molecular plane with respect to the layer's plane. Three trajectories corresponding to the parallel ($\phi_0 = 0°$), perpendicular ($\phi_0 = 90°$) and intermediate ($\phi_0 = 45°$) initial orientation are presented in Fig. 1 through the time–potential energy dependences. In each case, the final states have nearly the same potential energy and correspond to the same equilibrium state that is characterized by a parallel orientation $\phi_0 = 0°$. For $\phi_0 \neq 0°$ orientations there exists a kind of intermediate equilibrium with non-zero angle ϕ for which two major dynamical time scales exist, one corresponding to a movement perpendicular to the surface and another corresponding to rotation around the equilibrium parallel state. The direction of a molecule with respect to the axes of the surface's cell is also significant but, due to the relatively large dimensionality of stilbene with respect to the cell's period, the corresponding potential energy dependence is weak. Its minimization requires much more calculation time than we had and prevented us therefore from a complete minimization (in the minimization procedure we have used a damping time $\tau_r = 1.0$ ps).

3. CALCULATION OF THE ABSORPTION SPECTRUM OF SURFACE-ADSORBED *cis*-STILBENE

For systems with a few degrees of freedom an exact (numerically) fully quantum treatment is feasible. More complicated systems like a polyatomic molecule on surface require the introduction of statistical methods. Here we use the density
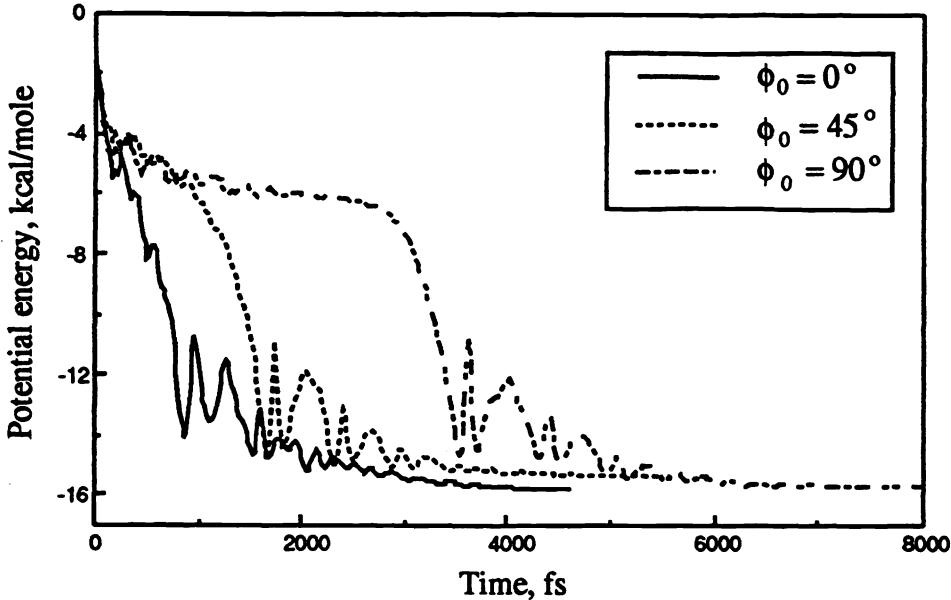
Figure 1: Calculation of the equilibrium state of *cis*-stilbene molecule on the surface. Time dependence of the molecule's potential energy. Damping rate is equal to 1 ps, ϕ is an orientation angle with respect to the surface.

matrix formalism[6-9] which allows the introduction of nonessential "bath" degrees of freedom, carrying out of thermal averagings and mixed quantum and classical description of different degrees of freedom. For example, the essential object in this study is the molecule and the surface is providing a "bath" of interactions.

Utilizing the interaction representation[7] for the molecular system interacting with a laser field, the density matrix of the excited state is given by[1]

$$\hat{\rho}_e = \frac{|d_{ge}|^2}{4\hbar^2} \int\int d\tau_1 d\tau_2 E_L(\tau_1) E_L^*(\tau_2) \exp[-\frac{i}{\hbar}\hat{\mathcal{H}}_e(t-s)]\hat{\rho}_e^0(\tau)\exp[\frac{i}{\hbar}\hat{\mathcal{H}}_e(t-s)], \tag{3}$$

where we have used second order with respect to the field perturbation expansion and the Condon approximation for the electronic transition dipole moment, d_{ge}. In this equation $E_L(\tau_k)$ is the complex wavefunction of the laser field, $\tau = \tau_2 - \tau_1$; $s = (\tau_2 + \tau_1)/2$;

$$\hat{\rho}_e^0(\tau) = \exp(-\frac{i}{\hbar}\hat{\mathcal{H}}_e\tau/2)\exp(\frac{i}{\hbar}\hat{\mathcal{H}}_g\tau/2)\hat{\rho}_g^T \exp(\frac{i}{\hbar}\hat{\mathcal{H}}_g\tau/2)\exp(-\frac{i}{\hbar}\hat{\mathcal{H}}_e\tau/2), \tag{4}$$

and $\hat{\rho}_g^T$ is the density matrix of the ground equilibrium state with temperature T.

When the evolution of the density matrix is performed for the time scales of interest we obtain the absorption spectrum by averaging the final density matrix. In addition we obtain the average values and the distribution of the coordinates and momenta which can be used for further MD simulations of the excited state dynamics. In order to obtain analytical results we further invoke the harmonic approximation for the molecule.

If we consider a harmonic polyatomic molecule with two adiabatic electronic states $|g\rangle$ and $|e\rangle$ and N_v vibrational degrees of freedom, we can write the Hamiltonian (in the absence of an electromagnetic field and electronic relaxation) as

$$\mathcal{H} = |g\rangle\mathcal{H}_g\langle g| + |e\rangle(\hbar\omega_{ge} + \mathcal{H}_e)\langle e|, \tag{5}$$

with

$$\mathcal{H}_g = \frac{\hbar}{2}\sum_{j=1}^{N_v}\omega_j''(\hat{p}_j''^2 + \hat{q}_j''^2 - 1), \qquad \mathcal{H}_e = \frac{\hbar}{2}\sum_{j=1}^{N_v}\omega_j'(\hat{p}_j'^2 + \hat{q}_j'^2 - 1),$$

and where

$$\hat{q}' = S\hat{q}'' + \bar{D} \quad . \tag{6}$$

Here, ω_{ge} is the electronic transition frequency between the lowest vibronic states of $|g\rangle$ and $|e\rangle$ (0-0 transition), and we label ground-state quantities by a double prime and excited-state quantities by a single prime. In Eqs. (5,6) $\bar{p}'$ and $\bar{q}'$ denote the dimensionless normal mode momentum and position vectors, respectively, on the excited state. Likewise, $\bar{p}''$ and $\bar{q}''$ represent dimensionless normal mode momentum and position vectors on the ground state.

These vectors can be related to the dimensioned Cartesian displacement and momentum coordinates, (r, p), using the normal mode transformation for mass-weighted coordinates on the ground state. This gives (in matrix notation)

$$\bar{p}'' = \frac{1}{\hbar^{1/2}}\omega''^{-1/2} \cdot V \cdot M^{-1/2} \cdot p \quad , \qquad \bar{q}'' = \frac{1}{\hbar^{1/2}}\omega''^{1/2} \cdot V \cdot M^{1/2} \cdot r \,, \tag{7}$$

where ω'' and M are diagonal matrices whose elements are the normal mode frequencies and atomic masses, respectively, and V is the diagonalizing unitary transformation matrix that relates the Cartesian displacements, r, to the mass-weighted normal mode coordinates, Q'', that is,

$$Q'' = V \cdot M^{1/2} \cdot r \quad , \qquad P'' = V \cdot M^{-1/2} \cdot p. \tag{8}$$

We discard the six zero-frequency normal modes arising from translation and rotation to obtain $(3N - 6)$ normal mode coordinates.

In Eq. (6), S is the Dushinsky rotation matrix which allows the ground and excited state normal coordinates to be different. If the normal modes in the ground and the electronically excited states are identical, the Dushinsky transformation matrix is diagonal, that is,

$$S_{ij} = \left(\frac{\omega_i'}{\omega_j''}\right)\delta_{ij}, \tag{9}$$

and the transformation between the normal coordinates is

$$Q' = Q'' + D \quad . \tag{10}$$

where $\bar{D}$ in Eq. (6) is the dimensionless displacement between the equilibrium configurations of the two electronic states. Its components $\bar{D}_j$ are related to D_j by

$$\bar{D}_j = \left(\frac{\omega_j'}{\hbar}\right)^{1/2} D_j \quad . \tag{11}$$

With the harmonic Hamiltonian defined with Eq. 5, Eq. 4 determines a generalized Gaussian density matrix and using standard techniques for calculation of averages, analytical expressions can be obtained for the quantities of interest. The absorption (excitation) or 0^0 dispersed fluorescence spectra (0^0 denotes the vibrationless excited electronic state) of the molecule are calculated in the dipole and Condon approximation using the following formula for the transition probability:[1-3]

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

where $f_p(\tau) = \int ds u_p(s - \tau/2)u_p^*(s + \tau/2)$ is the laser pulse autocorrelation function; $\Omega_L = E_L d_{ge}/\hbar$ is the Rabi frequency; $\chi(\tau)$ is the linear response function given by[1-3]

$$\chi(\tau) = \mathrm{Tr}\hat{\rho}_e^0(\tau) = \frac{\det[\sinh(\hbar\omega''/kT)/(s_1 s_2)]}{\det^{1/2}(c_1/\omega'' + c_2/\omega')\det^{1/2}(c_1\omega'' + c_2\omega')} \times$$

$$\times \exp[-\frac{1}{\hbar}D^T \cdot (c_1/\omega'' + c_2/\omega')^{-1} \cdot D], \tag{13}$$

$$s_1 = \sinh[\omega''(\hbar/kT - i\tau)], \qquad s_2 = \sinh(i\omega'\tau/2),$$

$$c_1 = \coth[\omega''(\hbar/kT - i\tau)/2], \qquad c_2 = \coth(i\omega'\tau/2).$$

Here the matrices ω'' and ω' are diagonal when the Dushinsky rotation matrix is also diagonal, in accordance with Eq. (9). Eqs. (12,13) provide the quantum expression for the one-photon transition probability in terms of the ground

and excited state frequency matrices, the displacements of the two surfaces and the temperature, which is the complete set of parameters characterizing a harmonic molecule.

The general procedure for computing the electronic-vibrational spectra is as follows. First, the ground and excited states of the molecule are defined in the Born-Oppenheimer approximation using empirical MM approach and Eq. 2. The frequency matrices ω'' and ω', and the vector of displacements D are calculated using standard routines for normal mode analysis. Then, the temperature is given and the function $\chi(\tau)$ is calculated using Eq. (13) for N points (N is set to an exact power of 2 for the use of a FFT routine—typically $N = 8192$) with time increments $\Delta\tau = [(N-1)\Delta\omega]^{-1}$, where $\Delta\omega$ is the spectral resolution of the calculation. A standard FFT routine is used to obtain the absorption spectrum via Eq. (12).

The calculated results for the absorption spectra obtained both for isolated and surface-adsorbed *trans*-stilbene molecule are presented in Fig. 2. The spectrum of the surface-adsorbed molecule at T=5° K is as sharp as the spectrum of isolated molecule. We investigated the structure of the spectrum as a function of the distance between the surface and the molecule introducing a scaling coefficient ξ. This provides us with the correlation between the lines of the isolated and surface-adsorbed species. The equilibrium structure of a molecule on the surface, obtained in Sec. 3, is described by $\xi = 1$ and the case of infinitely large distance (isolated molecule) between a molecule and the surface is described by $\xi = 0$. The correspondence between the spectral lines of isolated and surface-adsorbed trans-stilbene is also presented in Fig. 2. It shows that the corresponding frequencies of an adsorbed molecule are shifted to the violet edge due to the additional interaction with the surface.
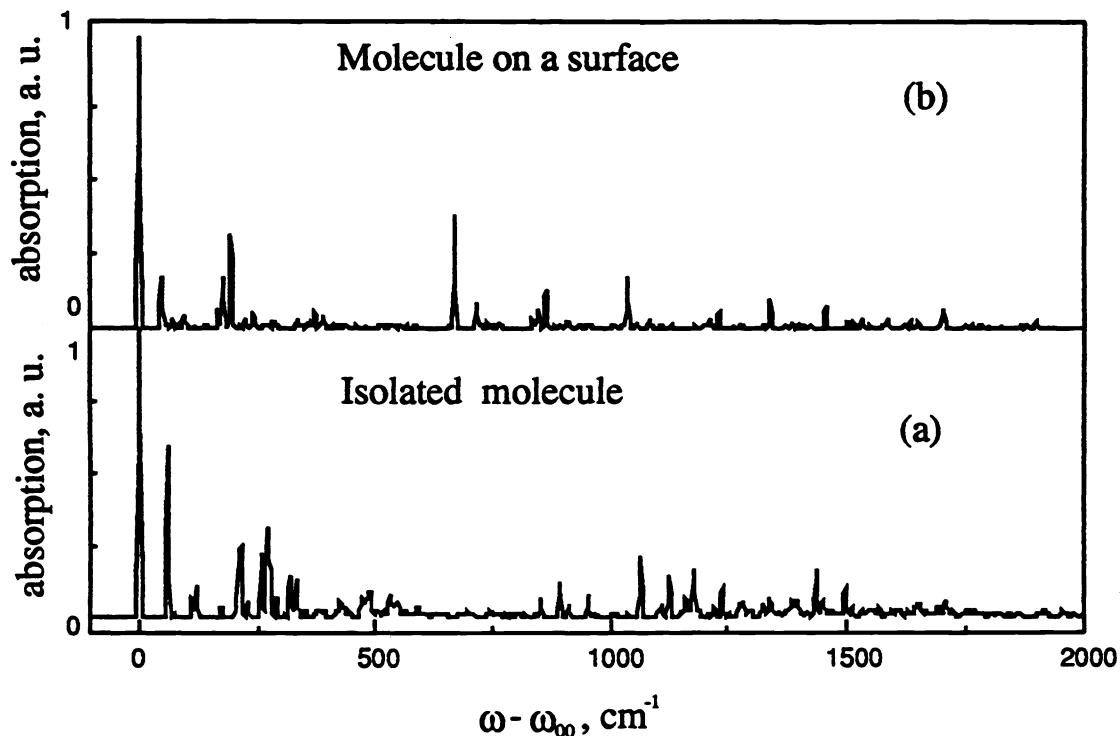

Figure 2: Calculated absorption spectra of (a) isolated and (b) surface-adsorbed *trans*-stilbene.

4. DYNAMICS OF PHOTOEXCITED SURFACE-ADSORBED *cis*-STILBENE

The excited state dynamics of *cis*-stilbene was modeled using an ensemble of classical trajectories. For the averaged normal coordinates after the excitation, we have

$$\mathbf{Q}'_{av} = \mathbf{Q}'_0 + \int p(\tau)\Delta\mathbf{Q}(\tau)d\tau/P(\omega_L), \qquad (14)$$

where $\mathbf{Q}'_0$ is the minimum energy configuration on the excited electronic state $|e\rangle$; $p(\tau)$ is the time-density expression, $dP(\omega_L)/d\tau$ (see Eq. (12)); and $\Delta\mathbf{Q}(\tau)$ is the (dynamical) displacement vector corresponding to time interval τ and given by[1-3]

$$\Delta\mathbf{Q}(\tau) = \frac{\mathrm{Tr}\Delta\hat{Q}\hat{\rho}^0_e(\tau)}{\mathrm{Tr}\hat{\rho}^0_e(\tau)} = -\omega'^{-1}\mathbf{s}_2^{-1}(c_1/\omega'' + c_2/\omega')^{-1}\mathbf{D} \quad . \qquad (15)$$

On average the momenta are not changed during the excitation because the Hamiltonians $\mathcal{H}_g$ and $\mathcal{H}_e$ are displaced from each other only in coordinate space, and not in momentum space. The main innovation presented here is the use of the results for harmonic potentials to generate a method for creating quasiclassical initial conditions that simulate the nonstationary state prepared by an ultrashort pulse for a molecule at finite (non-zero) temperature.

The initial conditions for the trajectory calculations were chosen to reflect the quantum state prepared by excitation of a vibrationally cold harmonic molecule using an ultrashort laser pulse. Using the empirical PES of the surface adsorbed molecule for the ground and excited states, the frequency matrices and displacements were calculated for all 72 normal modes. Then excitation with a 100 fs Gaussian laser pulse with 4000 cm^{-1} excess vibrational energy was modeled in the way similar to Ref. 3. Here we present the calculation results for the dynamics on the excited electronic surface. Typical trajectories are presented in Fig. 3. They show that an adsorbed molecule moves to the twisted state about 2 times faster than an isolated one. The corresponding average time to achieve the 90° twisted configuration is $\tau_p \sim 140$ fs; whereas, in the case of an isolated molecule it is ~ 280 fs. Thus, under similar excitation conditions, the surface–molecule interaction accelerates the isomerization process relative to that in the isolated molecule.

Finally, the dynamics of one of the two phenyl rings' twist angles $\phi(C_{ph1}C_eC_eC_{ph2})$ is presented in Fig. 3, (c). As in an isolated molecule the phenyl ring undergoes torsional rotation, however, in adsorbed stilbene it undergoes additional adjustments so as to achieve a final state nearly parallel to the surface.

5. CONCLUSIONS

Using harmonic approximation of the PES and the calculation methods of Refs. (1–3), we have calculated the absorption spectra and photoinduced dynamics of surface-adsorbed *trans*-stilbene molecule. Although just the simplest model of a molecule-surface interaction with a graphite lattice was used, we expect that the correspondence between the spectra lines of an isolated molecule and adsorbed one, revealed in our calculations, is qualitatively correct.

Using the MM method we have also calculated the isomerization dynamics of a photoexcited surface-adsorbed *cis*-stilbene molecule and discovered that it proceeds ~ 2 times faster than in case of isolated stilbene. The average time for the transition to the 90° twisted configuration is equal to ~ 140 fs. An analysis of the calculated trajectories shows that the influence of a graphite lattice does not relax the ability to undergo *cis-trans* photoisomerization.

We are also able now to modify our calculations in order to take into account specific lattice vibrations. That will enable us to describe dynamical interplay between a molecule and the lattice and provide the calculated spectra including the influence of interaction of molecule vibrations with surface phonons. The computer simulation undertaken in this work shows that such a generalization is possible with use of the available computer resources.
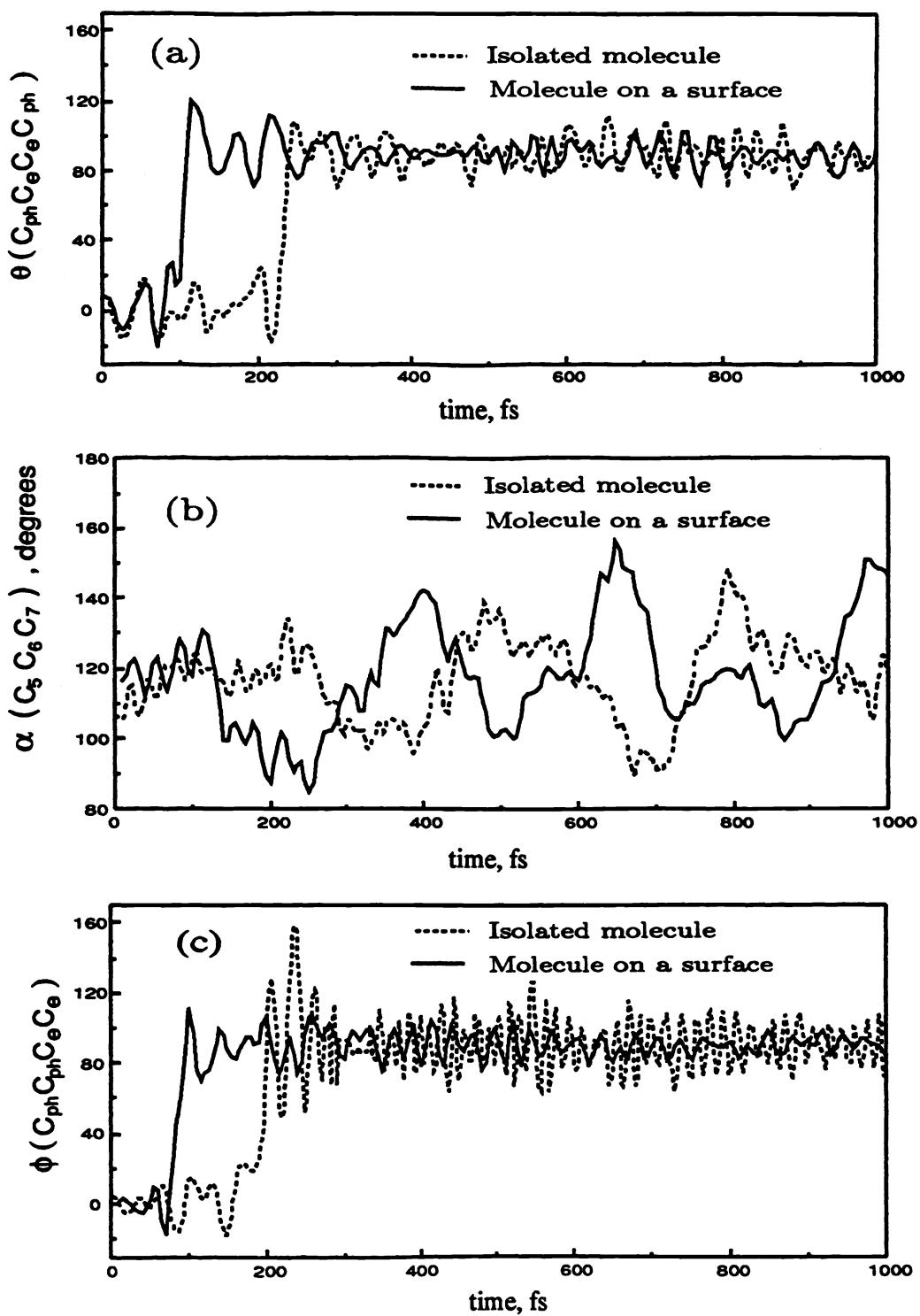
6. ACKNOWLEDGMENTS

Figure 3: Time dependence of (a) torsional angle $\theta(C_{ph}C_eC_eC_{ph})$, (b) bending angle $\alpha(C_5C_6C_7)$ and (c) phenyl twist angle $\phi(C_{ph1}C_eC_eC_{ph2})$ calculated along a representative single MD trajectory cis-stilbene ($\pm 180°$ angles are geometreically identical).

REFERENCES

1. B.A.Grishanin, V.D.Vachev, V.N.Zadkov, *Mol. Cryst. Liq. Cryst.*, Vol. 3, pp. 375–386 (1992).

2. V.D.Vachev, J.H.Frederick, B.A.Grishanin, V.N.Zadkov, N.I.Koroteev, *Chem. Phys. Lett.*, Vol. 215, pp. 306–314 (1993).

3. V. D. Vachev, J. H. Frederick, B. A. Grishanin, V. N. Zadkov, N. I. Koroteev, *J. Phys. Chem.*, Vol. 99, pp. 5247–5263 (1995).

4. P. Ye, Y. R. Shen, *Phys. Rev.*, Vol. B28, No. 8, pp.4288–4294 (1983).

5. T. L. Hill, *J. Chem. Phys.*, Vol. 16, pp. 399–404 (1948).

6. U. Fano, *Rev. Mod. Phys.*, Vol. 29, pp. 74–93 (1957).

7. R. P. Feynman, *Phys. Rev.*, Vol. 84, pp. 108–128 (1951).

8. L. E. Fried, S. Mukamel, *Adv. Chem. Phys.*, Vol. 84, pp. 435–516 (1993).

9. S. Mukamel, *Annu. Rev. Phys. Chem.*, Vol. 41, pp. 647–681 (1990).