

Dynamics of the photoinduced ring-opening of stilbene, a prototypical diarylethene

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Abstract

Simulations of the photoconversion of 4a,4b-dihydrophenanthrene (DHP) to stilbene, using semiclassical electron-radiation-ion dynamics, are reported. The carbon single bond connecting the phenyl rings breaks approximately 200 fs after the laser pulse is turned off. In the results shown here, the excited *cis*-stilbene molecule then further isomerizes to the *trans* conformation after about 1 ps. Each of these two changes of molecular geometry involves a HOMO–LUMO avoided crossing, which produces a transfer of electronic population from LUMO to HOMO. These detailed dynamical simulations are consistent with the interpretation that ring-opening in stilbene is a single photon process.

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1. Introduction

Derivatives of diarylethenes, especially those with thiophene rings, are currently being investigated as candidates for switches in molecular electronic devices, or for other applications, because of their photochromic properties [1–6]. In these molecules ring-opening is induced with visible light, and the reverse process by UV radiation. Various derivatives exhibit enhanced thermal stability, quantum yield, and response time, and also decreased fatigue [7]. In solution, the photocyclization process has a higher quantum yield than the ring-opening process [1]. Quantum molecular dynamics calculations performed by Sankey and coworkers on dithienylethene derivatives [8] have shown that the ring-closing mechanism involves a swapping of the HOMO and LUMO during bond formation. Similar calculations were unable to yield the reverse ring-opening process. Since the photoinduced electronic transitions were modeled by moving an electron from the HOMO into the LUMO, without the possibility of transitions to and from other orbitals during the absorption process, the authors suggested that the photoreversion process may involve

multiphoton transitions. This suggestion is in accord with previous ideas, based on both picosecond experimental studies [5] and *ab initio* complete-active-space self-consistent-field (CASSCF) potential energy surface calculations [9]. A theoretical study of a hydrocarbon model system, using the molecular mechanics valence bond method (MMVB), has located a conical intersection (CI) between the ground state and lowest excited state surfaces, but has also indicated that this CI is only dynamically accessible [10].

Here we present dynamical simulations that allow for *n* photon processes along the ring-opening pathway in stilbene, a well-studied diarylethene. The photoinduced *cis* to *trans* isomerization process has been investigated in detail by our group [11,12] and others [13]. The competing process, *cis* to the closed-ring structure 4a,4b-dihydrophenanthrene (DHP), has received more limited attention, perhaps because of its lower quantum yield. Experiments indicate that 70% of excited *cis*-stilbene molecules isomerize to the *trans* form, while only 30% isomerize to DHP [14]. It been shown that upon irradiation with 436 nm light, DHP is converted to *cis*-stilbene with a quantum yield of 0.66 [15].

Although stilbene is not a viable candidate for a molecular switch, since DHP undergoes an irreversible

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transformation to phenanthrene in the presence of oxygen [7], we study the photocyclization/reversion processes in this prototypical molecule in order to lay the ground work for future studies of more realistic model dithienylethenes. Our group has previously shown that ring-closure involves avoided crossings between HOMO and LUMO levels, with a subsequent depopulation of the LUMO [16]. The present work shows that the reverse process, ring-opening, also proceeds via a transfer of electronic population from LUMO to HOMO, without substantial transfer to or from other orbitals.

2. Methodology

The simulations presented here employ semiclassical electron-radiation-ion dynamics (SERID), a method described in Ref. [17]. The nuclei and radiation field are treated classically, while the time-dependent Schrödinger equation is solved at each time step, in a nonorthogonal basis, to obtain the one-electron states. The Hamiltonian and overlap matrix, and the effective ion–ion repulsion, are determined by parameters previously fitted to density-functional calculations [18]. As in any semiclassical theory, one observes effective ‘*n*-photon’ and ‘*n*-phonon’ processes. Various kinds of transitions are observed, including those from one excited state to another. The laser pulse is coupled to the electrons through the Peierls substitution.

$$H_{ab}(\mathbf{X} - \mathbf{X}') = H_{ab}^0(\mathbf{X} - \mathbf{X}') \exp(iq/\hbar c \mathbf{A}(t) \cdot (\mathbf{X} - \mathbf{X}')),$$

where $\mathbf{A}(t)$ is the vector potential and the \mathbf{X} are nuclear coordinates.

For comparison, we have also performed density-functional theory (DFT) calculations using the GAUSSIAN 03 package [19] with the B3LYP functional and the 6-311G(d,p) basis set.

3. Results

3.1. Equilibrium structures

The initial geometries of both the open and closed forms of stilbene were determined by performing simulations (lasting 4000 fs) in which the velocity of each atom was

reduced by 0.03% after each time step (of 10 as). The bond lengths and bond angles agree very well with density-functional theory calculations, as can be seen in Fig. 1. The DHP molecule is 1.11 eV higher in energy than the *cis*-stilbene molecule (compared with an energy difference of 1.73 eV in the DFT calculations). Both molecules have C_2 symmetry in the ground state. The energies and symmetries for the orbitals of both *cis*-stilbene and DHP near the HOMO–LUMO gap are summarized in Table 1. A comparison with DFT calculations shows qualitatively similar molecular orbital ordering, symmetries, and energies. In both cases, there is a switching of the symmetry of the HOMO and LUMO orbitals between the open and closed molecules. This behavior was also seen in model dithienylethene systems [8].

The above procedure defines an initial zero temperature equilibrium geometry for each of the molecules. In order to include thermal effects, we then ran a 2000 fs simulation at room-temperature (again with a 10 as timestep) for each molecule. Temperature is included in the simulations through initial random velocities that are scaled so that the total kinetic energy is equal to $(3N - 3)kT/2$, where N is the number of atoms, k the Boltzmann constant, and T the temperature. Although bond lengths and molecular orbital energies fluctuate about their ground state values, at no time during the 2000 fs simulation did either molecule change configuration. This indicates that the isomerization seen in the simulations described below is not a result of thermal motion alone. The final nuclear positions and velocities (and corresponding electronic states) were then used as the initial conditions for the excited state simulations.

3.2. Ring-opening dynamics of DHP

Time-dependent density-functional theory (TDDFT) calculations predict that the first singlet transition in DHP is a HOMO to LUMO transition corresponding to a photon energy of 2.45 eV [20]. (TDDFT often gives poor results for electronic absorption spectra, as one might expect, since DFT was originally proposed as a ground state theory and is known to be unreliable for excitation energies, even when the ‘functional’ – i.e., the potential

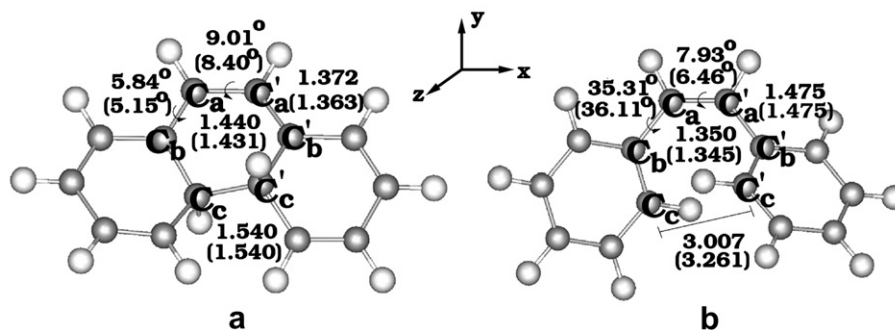


Fig. 1. Equilibrium geometry of: (a) DHP and (b) *cis*-stilbene. The relevant SERID bonds and angles are shown, and can be compared with the corresponding B3LYP/6-311G(d,p) results, given in parenthesis.

Table 1
Molecular orbital energies and symmetries calculated with SERID and B3LYP/6-311G(d,p) for the ground state geometry of *cis*-stilbene and DHP

Level	<i>cis</i> SERID (eV)	<i>cis</i> DFT (eV)	<i>cis</i> Symmetry	DHP SERID (eV)	DHP DFT (eV)	DHP symmetry
HOMO–3	–7.36	–7.21	A	–7.69	–8.33	B
HOMO–2	–7.26	–7.06	A	–7.52	–7.38	A
HOMO–1	–7.24	–6.91	B	–6.62	–6.23	B
HOMO	–6.38	–5.95	B	–5.36	–4.94	A
LUMO	–3.00	–1.41	A	–3.74	–2.14	B
LUMO+1	–2.04	–0.44	A	–2.62	–0.84	A
LUMO+2	–1.90	–0.10	B	–1.49	0.00	B
LUMO+3	–1.78	–0.02	B	–0.29	1.20	A

used to model exchange and correlation effects – includes parameters that are fitted to experimental excitation energies. However, TDDFT studies have proved rather successful in understanding the kinds of problems considered here, involving excitations and conformational changes in stilbene [20–22].) In order to determine whether the SERID simulations also predict a HOMO to LUMO transition, we subjected the room-temperature equilibrated DHP molecule to a 150 fs (FWHM) pulse, with a fluence of 2.68 kJ/m² and a photon energy of 1.6 eV, having a polarization in the (1,1,1) direction with respect to the coordinates of Fig. 1. (This photon energy is matched to the SERID HOMO–LUMO gap, so that HOMO to LUMO is a one-photon transition. It should be emphasized that the present approach provides a reasonably reliable method for addressing qualitative issues involved in the response of electrons and nuclei to a femtosecond-scale laser pulse, but does not yield quantitatively accurate predictions of the electronic excitation energies. It should also be noted that a quantitative comparison between these simulations and experiment would require averaging over many initial conditions and polarization vectors.) The total simulation time was 4000 fs, with a time step of 5 as.

The geometrical changes in Fig. 2 clearly shows a ring-opening event, followed by a further *cis* to *trans* isomerization approximately 1 ps later. The initial breaking of the C_c–C_{c'} bond (the bond connecting the two phenyl rings) occurs at about 520 fs, approximately 200 fs after the completion of the laser pulse. At 598 fs, the distance

between these two carbon atoms has increased to 3.00 Å, the equilibrium distance in the ground state *cis*-stilbene molecule (see Fig. 2a). The dihedral angle formed by C_b–C_a–C_{a'}–C_{b'}, called θ in the remainder of this Letter, fluctuates around an angle near 0° (ground state equilibrium values are $\theta_{\text{DHP}} = 9.01^\circ$ and $\theta_{\text{cis}} = 7.93^\circ$) until roughly 1560 fs, at which time θ steadily increases until it reaches a value of 180° at 1828 fs, indicating that the molecule is in the *trans* configuration (see Fig. 2b). It oscillates around this value for the remainder of the simulation.

The changes in molecular geometry result from forces that are due to changes in the populations of electronic states. Both the ring-opening and the subsequent *cis*–*trans* isomerization are associated with close avoided crossings of the HOMO and LUMO levels, which lead to transfer of electronic population from LUMO to HOMO. Fig. 3 gives an overview of the HOMO–3 through LUMO+3 orbital energies (Fig. 3a) and population of the HOMO and LUMO orbitals (Fig. 3b) for the entire duration of the simulation. At the end of the laser pulse ($t = 300$ fs), the populations of the HOMO and LUMO states are, respectively, 1.34 and 0.94 electrons. Roughly one electron has been transferred from the HOMO to the LUMO by the laser pulse, in agreement with TDDFT calculations. There are also small excitations out of the lower-lying occupied orbitals and into higher lying unoccupied orbitals, which are not shown here, since they play a negligible role in the dynamics of the molecule.

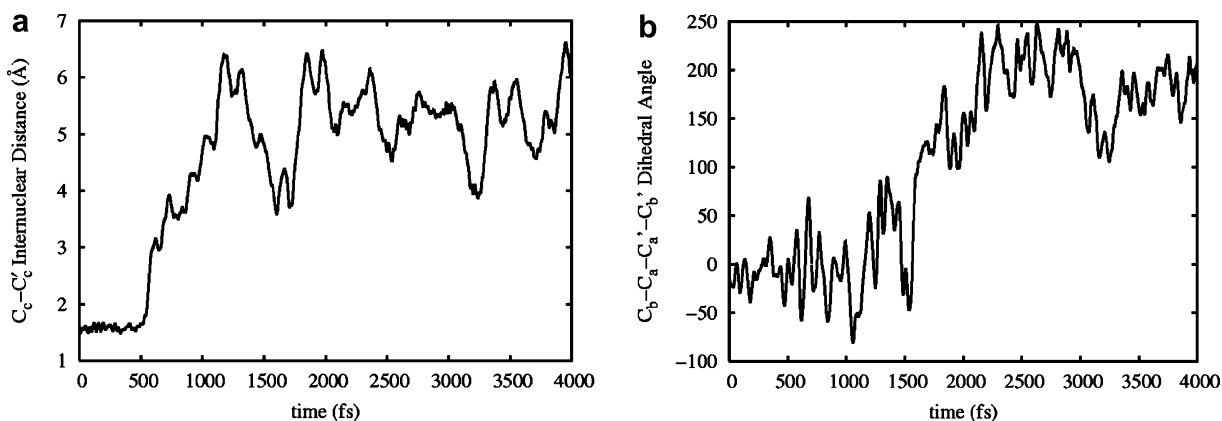


Fig. 2. Time dependence of: (a) C_c–C_{c'} internuclear separation and (b) C_b–C_a–C_{a'}–C_{b'} dihedral angle in a DHP molecule subjected to a 150 fs (FWHM) pulse with a photon energy of 1.6 eV and a fluence of 2.68 kJ/m². The labeling of atoms is defined in Fig. 1.

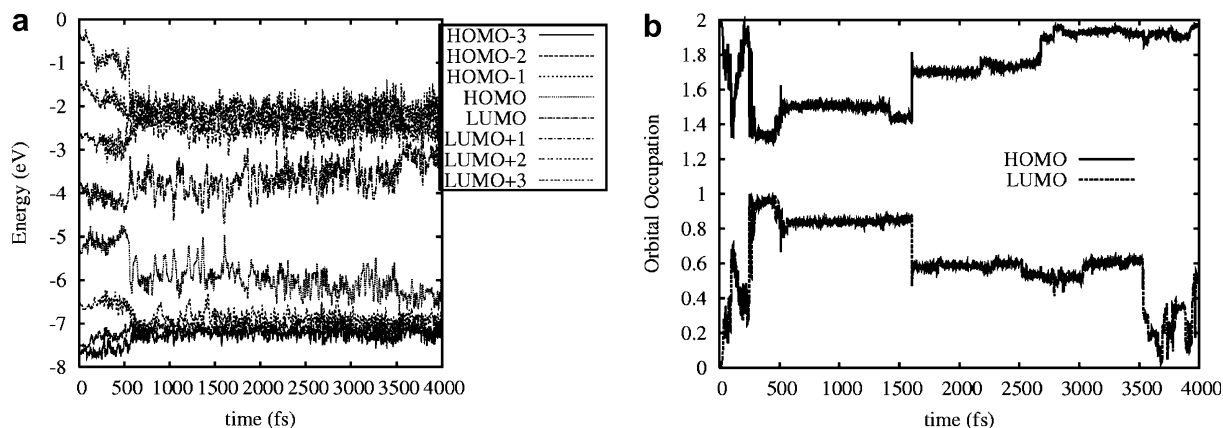


Fig. 3. (a) HOMO – 3 through LUMO + 3 orbital energies and (b) HOMO and LUMO orbital populations, monitored for the entire 4000 fs simulation. A 300 fs (full-duration) laser pulse with a frequency of 1.6 eV and a fluence of 2.68 kJ/m² is applied at time $t = 0$.

There are two major sets of LUMO to HOMO transitions after the completion of the laser pulse. The first occurs immediately before the $C_c-C'_c$ bond breaks, transferring roughly 0.15 electrons back into the HOMO. There is then a substantial change in the configuration of the orbitals surrounding the HOMO–LUMO gap, during the change from DHP to *cis*-stilbene (Fig. 3a). This reconfiguration, associated with bond breaking, occurs over the relatively long time scale of approximately 100 fs, following the transitions from LUMO to HOMO, which begin at about 440 fs (see Fig. 4b).

The second major set of transitions occurs at the time of the *cis* to *trans* isomerization, transferring roughly another 0.25 electrons out of the LUMO level when θ approaches 90° (see Fig. 2b). These results are complementary to potential energy surface calculations, in which a conical intersection exists between the S_0 and S_1 surfaces at a similar dihedral angle [13]. Our group has previously presented detailed simulations of this transition [11,12].

Further population changes (including the decrease in LUMO occupancy between 3500 and 4000 fs) are due primarily to population transfers among the states above the

HOMO–LUMO gap, and among those below this gap, rather than transitions across the gap.

Since a small electronic population remains in excited states, the molecule is not in the ground state geometry at the end of the simulation. Nevertheless, we still observe the tendency of the molecule to return to an equilibrium configuration. Upon laser pulse excitation, both the vinyl ($C_a-C'_a$) single bond and the two vinyl–phenyl (C_a-C_b) double bonds in the DHP molecule tend to elongate. After depopulation of the LUMO level, the vinyl bond shortens (see Fig. 5a), whereas the two vinyl–phenyl bonds remain elongated (see Fig. 5b). This behavior is in agreement with the calculated ground state geometries, in which the vinyl bond in DHP is a single bond, the vinyl bond in *cis*-stilbene is a double bond, the two phenyl–vinyl bonds in DHP are double bonds, and the two phenyl–vinyl bonds in *cis*-stilbene are single bonds. It is associated with the swapping of the HOMO and LUMO orbitals during isomerization.

It should be emphasized that isomerization does not necessarily accompany ring-opening. In other simulations, most of which were followed in less detail, we have observed essentially every possible combination of events,

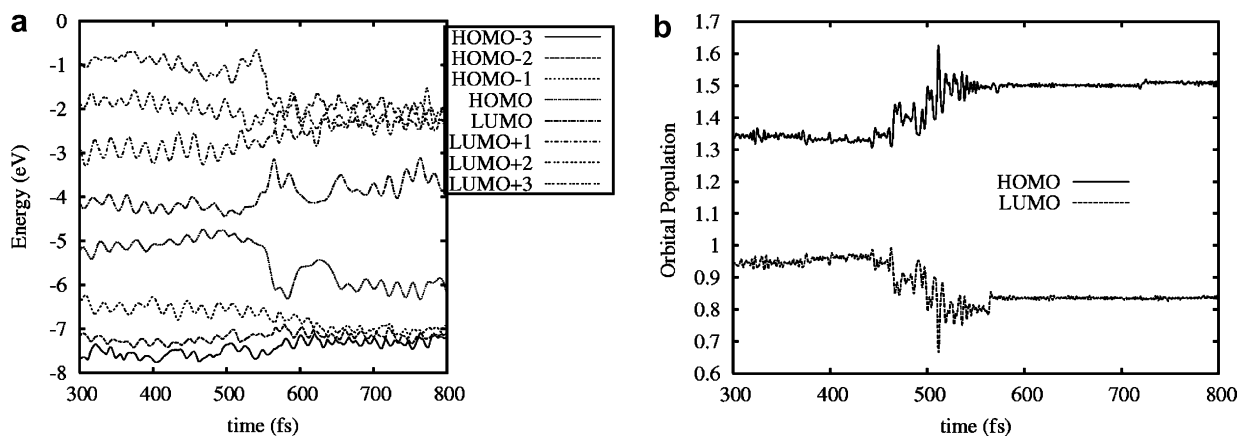


Fig. 4. Detailed behavior of: (a) HOMO – 3 through LUMO + 3 orbital energies and (b) HOMO and LUMO orbital populations during breaking of the $C_c-C'_c$ bond in the time interval of 300 fs to 800 fs after the onset of the laser pulse.

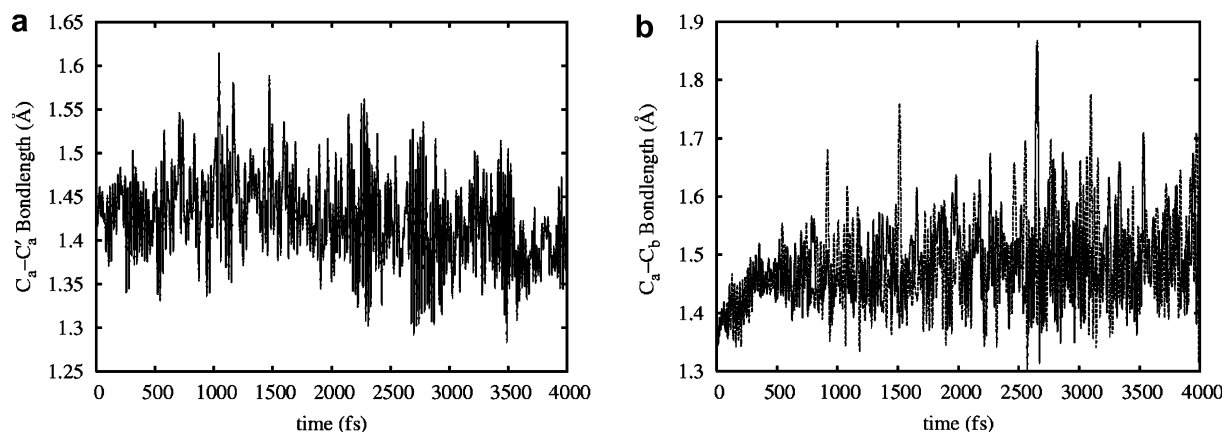


Fig. 5. (a) $C_a-C'_a$ and (b) C_a-C_b bonds in an initial DHP molecule subjected to a 150 fs (FWHM) pulse with a photon energy of 1.6 eV and a fluence of 2.68 kJ/m^2 .

including ring-opening without isomerization. But, the present simulation was chosen for detailed analysis because it provides a rather clear demonstration of both of these interesting processes: ring-opening and *cis-trans* isomerization.

4. Conclusions

We have performed semiclassical electron-radiation-ion dynamics simulations, in which the photoexcitation is explicitly included. After the completion of a 150 fs (FWHM) laser pulse, the bond connecting the two phenyl rings in DHP is broken within ~ 200 fs. In the results shown here, the *cis*-stilbene molecule then further isomerizes to the *trans* form, ~ 1 ps after the ring-opening event. Cycloreversion in the stilbene molecule thus requires only a single photon transition from the ground state into the lowest excited state, without significant transitions to higher excited states. Although stilbene and its thiol-substituted derivatives have many structural and electronic similarities, the nature of the ring-opening event in these dithienylethenes still needs to be investigated.

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References

- [1] M. Irie, T. Fukaminato, T. Sasaki, N. Tamai, T. Kawai, *Nature* 420 (2002) 759.
- [2] H. Miyasaka, T. Nobuto, A. Itaya, N. Tamai, M. Irie, *Chem. Phys. Lett.* 269 (1997) 281.
- [3] J. Ern et al., *Chem. Phys.* 246 (1999) 115.
- [4] J. Ern, A.T. Bens, H.-D. Martin, K. Kuldova, H.P. Trommsdorff, C. Kryschi, *J. Phys. Chem.* 106 (2002) 1654.
- [5] H. Miyasaka, M. Murakami, A. Itaya, D. Guillaumont, S. Nakamura, M. Irie, *J. Am. Chem. Soc.* 123 (2001) 753.
- [6] D. Dulic et al., *Phys. Rev. Lett.* 91 (2003) 207402.
- [7] M. Irie, *Chem. Rev.* 100 (2000) 1685.
- [8] J. Li, G. Speyer, O.F. Sankey, *Phys. Rev. Lett.* 93 (2004) 248302.
- [9] D. Guillaumont et al., *J. Phys. Chem. A* 106 (2002) 7222.
- [10] M. Boggio-Pasqua, M. Ravaglia, M.J. Bearpark, M. Garavelli, M.A. Robb, *J. Phys. Chem. A* 107 (2003) 11139.
- [11] Y. Dou, R.E. Allen, *J. Chem. Phys.* 119 (2003) 10658.
- [12] Y. Dou, R.E. Allen, *Chem. Phys. Lett.* 378 (2003) 323.
- [13] A good review of the literature can be found in D.H. Waldeck, *Chem. Rev.* 91 (1991) 415.
- [14] H. Petek, K. Yoshihara, Y. Fujiwara, Z. Lin, J.H. Penn, J.H. Frederick, *J. Phys. Chem.* 94 (1990) 7539.
- [15] K.A. Muszkat, E. Fischer, *J. Chem. Soc. B* (1967) 662.
- [16] Y. Dou, R.E. Allen, *J. Mod. Opt.* 51 (2004) 2485.
- [17] Y. Dou, B.R. Torralva, R.E. Allen, *J. Mod. Optics* 50 (2003) 2615.
- [18] D. Porezag, Th. Frauenheim, Th. Koehler, G. Seifert, R. Kaschner, *Phys. Rev. B* 51 (1995) 12947.
- [19] M.J. Frisch et al., GAUSSIAN 03, Revision C.02, Gaussian, Inc., Wallingford CT, 2004.
- [20] A.E. Clark, *J. Phys. Chem. A* 110 (2006) 3790.
- [21] R. Improta, F. Santoro, C. Dieltl, E. Papastathopoulos, G. Berber, *Chem. Phys. Lett.* 387 (2004) 509.
- [22] R. Improta, F. Santoro, *J. Phys. Chem. A* 109 (2005) 10058.