

Femtosecond-scale photodissociation of benzene

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Semiclassical electron-radiation-ion dynamics (SERID) has been used to calculate the bondlengths, HOMO-LUMO energy gap, and vibrational modes of benzene, and to examine the photodissociation of benzene molecules subjected to fast intense laser pulses. The calculated ground-state properties are in good agreement with experiment, confirming that density-functional-based SERID simulations provide a reliable treatment of bonding. We show results for representative simulations of the response of benzene to femtosecond-scale laser pulses, at various fluences corresponding to no dissociation, partial dissociation, and complete dissociation into atomic constituents.

1 Motivation

The response of complex molecules to femtosecond-scale laser pulses is important in many different contexts. As one example, we mention the detection of pathogens with techniques like FAST CARS [1]. One would like to understand the microscopic processes that transpire when a molecule like dipicolinic acid is subjected to an ultrafast laser pulse, including both the processes relevant to spectroscopy and those which may be involved in photochemical reactions at such high intensities.

In the present paper we report calculations for a slightly simpler molecule, benzene (C_6H_6), using semiclassical electron-radiation-ion dynamics (SERID), a technique for treating the response of electrons and nuclei in a molecule subjected to a radiation field [2–5]. Our principal goal in the work reported here is to determine the reliability of this technique for (1) calculating vibrational modes (which are of central importance in spectroscopy) and (2) studying the microscopic processes involved in femtosecond-scale photodissociation (which are obviously relevant to potential photoinduced changes in a sample being

studied with high-intensity laser pulses). Benzene was chosen because it is representative of the carbon-based ring structures that occur prominently in biological systems. There have been many experimental investigations related to various aspects of the photodissociation of benzene, including the hot benzene mechanism [6-11], lifetime measurements [12-15], pioneering photolysis studies [16-21], UV dissociation [22-29], and visible and IR dissociation [30-37], as well as computational work [38].

2 Method

As mentioned above, semiclassical electron-radiation-ion dynamics (SERID) is a technique for simulating the coupled dynamics of electrons and nuclei (or ion cores) when a molecule or material is subjected to a radiation field. The limiting approximation is this: Although the electrons are in time-dependent quantum states, both the radiation field and the motion of the nuclei are treated classically.

A semiclassical treatment of the radiation field still produces effective n -photon transitions corresponding to absorption and stimulated emission (as can be seen in n th-order time-dependent perturbation theory), but omits spontaneous emission due to quantum fluctuations of the radiation field. A semiclassical treatment of the nuclear motion similarly can produce effective n -phonon transitions corresponding to absorption and stimulated emission of vibrational quanta, but omits the zero-point quantum motion of the nuclei. (We define photon and phonon to mean excitations of an arbitrary radiation or vibrational field, rather than only excitations with well-defined propagation vectors.)

Since a SERID simulation requires solving the time-dependent Schrödinger equation every 30-50 attoseconds, it would require a prohibitively large amount of computer time to perform the many thousands of simulations that would be necessary for a true statistical description of the response of an ensemble of large molecules to applied fields. (One can easily perform large number of simulations in models that assume classical potentials of interaction between the atoms, but classical potentials do not provide even a proper treatment of covalent bonding in the ground state, and they certainly cannot be used to treat electronic excitations.) For this reason, one performs representative simulations that are primarily meant to show, in microscopic detail, the processes that occur as nuclei and electrons respond in a characteristic way.

One can summarize the above comments by saying that a SERID simulation exhibits the representative or average response of a molecule or material to an applied perturbation. The goal is *understanding* of fundamental microscopic processes, and not quantitative reproduction of experimental data.

	r_{CC} (\AA)	r_{CH} (\AA)	$E_{\text{HOMO-LUMO}}$ (eV)
SERID	1.402	1.098	4.96
experiment	1.399	1.101	4.90

Table 1. Properties of benzene calculated with SERID, compared with experimental bondlengths [39] and excitation energy [40].

A_{1g}	ν_1	beat
A_{1g}	ν_2	breathing
A_{2g}	ν_3	twist
A_{2u}	ν_4	CH wag
B_{1u}	ν_5	CH stretch
B_{1u}	ν_6	CCC bend
B_{2g}	ν_7	CH wag
B_{2g}	ν_8	ring torsion
B_{2u}	ν_9	CC stretch
B_{2u}	ν_{10}	CH bend

Table 2. The normal modes of benzene with A and B symmetry.

SERID simulations are complementary to other approaches which use the traditional approximations of physics and chemistry, including Fermi's golden rule, the Franck-Condon principle, and the Born-Oppenheimer approximation. In particular, SERID simulations can be employed for intense fields, short time scales, and large molecules, without the assumption that processes are either adiabatic or diabatic. One loses certain aspects of a full quantum description, but gains the ability to treat highly nontrivial processes. Such processes are increasingly relevant as ultrafast and ultra-intense laser pulses are applied to complex systems in chemistry, biology, physics, and materials science.

3 Results

We first carried out room-temperature simulations for benzene without an applied radiation field. A 2000 fs run was performed, with a time step of 50 attoseconds, and values were then averaged over this time interval for the bondlengths and the gap between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The results, shown in Table 1, are in remarkably good agreement with experiment.

	Experiment [43] (cm^{-1})	SERID (cm^{-1})	Pulay et al. [41] (cm^{-1})	Miani et al. [42] (cm^{-1})
ν_1	3074	3055	3096	3049
ν_2	993	1119	993	995
ν_3	1350	1336	1358	1346
ν_4	674	651	667	677
ν_5	3057	3021	3052	3404
ν_6	1010	1018	1010	1015
ν_7	990	902	996	997
ν_8	707	684	701	708
ν_9	1309	1402	1307	1305
ν_{10}	1150	1152	1145	1163

Table 3. Computed and experimental fundamental frequencies of benzene. The calculations of Pulay et al. [41] were done at the Hartree-Fock level with a double-zeta basis set, and the results of Miani et al. [42] were obtained via density-functional calculations with the B3LYP functional and a TZ2P basis set.

	estimated harmonic [43] (cm^{-1})	Goodman et al. [43] (cm^{-1})
ν_1	3191	3191
ν_2	994	994
ν_3	1367	1367
ν_4	674	674
ν_5	3174	3166
ν_6	1010	1014
ν_7	990	990
ν_8	707	707
ν_9	1309	1309
ν_{10}	1150	1150

Table 4. Harmonic frequencies obtained by Goodman et al. [43], compared with estimated harmonic frequencies from experiment. A more complete comparison of harmonic frequencies can be found in the work of Martin et al. [44].

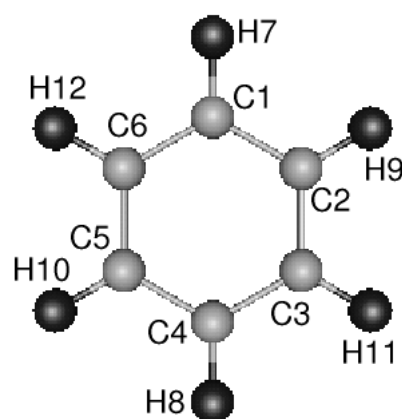


Figure 1. Initial coordinates of the equilibrated benzene molecule, prior to laser excitation.

We next calculated the frequencies for particular vibrational modes, using the following procedure: First the atoms in the molecule were assigned initial velocities corresponding to their motion in a selected mode. Then a SERID simulation was performed for 2000 fs. Finally the velocity autocorrelation function was calculated and Fourier-transformed to obtain the vibrational frequencies. As can be seen at <http://faculty.physics.tamu.edu/allen/benzene-modes/>, animations were also made which clearly exhibit the nature of each mode: breathing, beating (of H atoms against C atoms), twisting, etc.

The results for ten vibrational frequencies are shown in Tables 2-4. (The labeling of symmetries is standard, and we do not consider the E modes here.) It can be seen that there is good agreement between the SERID calculations and experimentally observed gas phase fundamental frequencies for every mode.

To summarize, the results of Tables 1-4 demonstrate that the technique used here, density-functional-based SERID, yields good results for ground-state bonding properties. This provides confidence in the use of the technique for simulations of the response of molecules to laser pulses.

We then performed such simulations, for initially-equilibrated benzene molecules subjected to laser pulses of various intensities. The labeling of atoms is shown in Fig. 1. As in earlier work [45], the vector potential is taken to have the time dependence

$$\mathbf{A}(t) = A_0 \cos\left(\frac{\pi(t - t_0/2)}{t_0}\right) \sin(\omega t), \quad 0 \leq t \leq t_0. \quad (1)$$

This form (i) closely resembles a Gaussian, (ii) clips the pulse to zero at beginning and end, (iii) gives zero slope for $A(t)^2$ at beginning and end, and (iv)

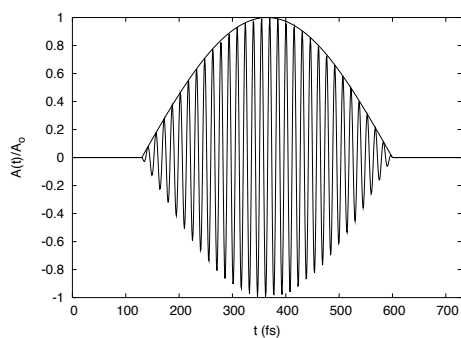


Figure 2. Pulse shape used in the present simulations, with the form given in Eq. (1).

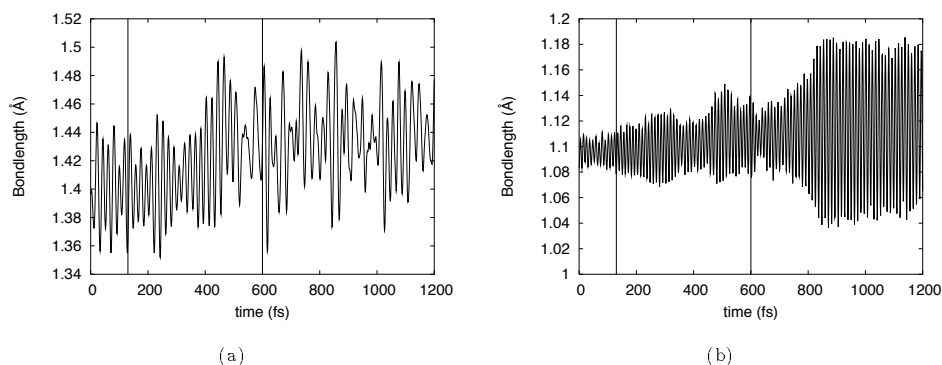


Figure 3. Average (a) CC bondlength and (b) CH bondlength for benzene excited by a 8.0 eV pulse with a duration of 470 fs and a fluence of 1.9 kJ/m². The vertical lines indicate the beginning and end of the Gaussian pulse.

gives a full-width at half-maximum (FWHM) duration for $A(t)^2$ of exactly half the total pulse time t_0 . A representative pulse is shown in Fig. 2.

In choosing parameters for the laser pulses, we follow the experimental studies of Farmanara et al. [26]. This group used 8.0 eV pulses with a total duration of 470 fs and an approximate pulse energy of 100 nJ. Since the laser fluence was low (approximately 0.04 kJ/m²) they did not observe fragmentation. Our goal here, on the other hand, was to observe the microscopic processes responsible for photodissociation, so we increased the fluences of the laser pulses in our simulations to much higher values, between 1.9 and 3.0 kJ/m². All of our calculations were done at room temperature, with the laser light polarized parallel to the initial direction of a CH bond. The simulation time was 1200 fs, with the pulse applied over the time interval between 130 and 600 fs. The photon energy (8.0 eV) is larger than the HOMO-LUMO gap of the molecule, so excitation can occur through one-photon absorption, and the results in-

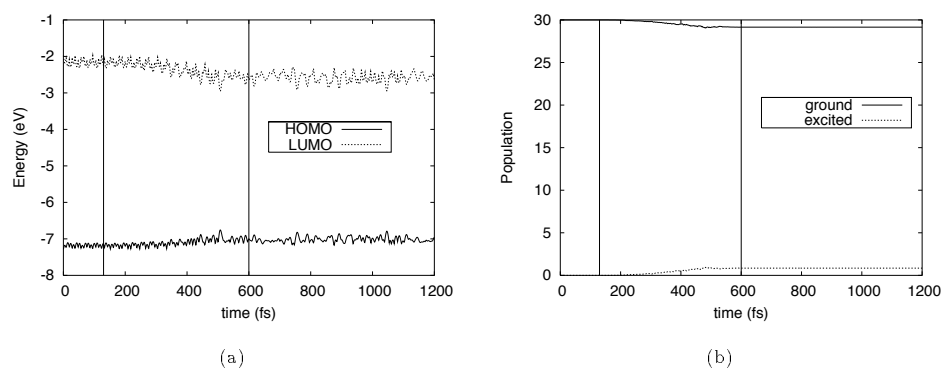


Figure 4. (a) Energy of the HOMO and LUMO levels of benzene excited by a laser pulse with the photon energy, duration, and fluence given in Fig. 3. (b) Population of the excited state and ground state in this same simulation. (Again, the vertical lines demarcate the duration of the laser pulse.)

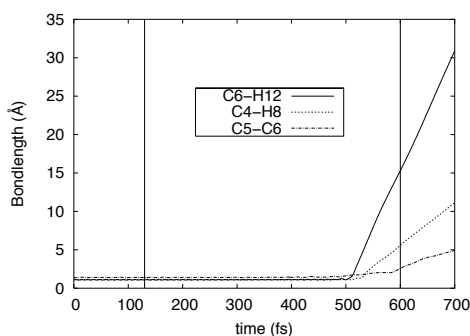


Figure 5. Time evolution of the two CH internuclear distances, and one CC internuclear distance, involved in the photodissociation of benzene subjected to an 8.0 eV light pulse with a total duration of 470 fs and a fluence of 2.3 kJ/m^2 . The vertical lines indicate the duration of the laser pulse.

indicate that multiphoton absorption is of minor importance with the present choice of laser pulse parameters.

At the lowest simulated fluence, 1.9 kJ/m^2 , we did not observe any bond breaking. Figures 3a and 3b show the typical CC and CH bond lengths as a function of time. After the laser pulse was turned off, the average CC and CH bond lengths were respectively 1.44 \AA and 1.11 \AA . The pulse did not significantly alter the energy of the HOMO or the LUMO energies, as can be seen in Fig. 4a, but it did pump approximately 3% of the electrons into the excited state, as shown in Fig 4b.

Increasing the laser fluence to 2.3 kJ/m^2 led to the onset of dissociation. After about 370 fs of pulse excitation, the molecule expelled two hydrogen

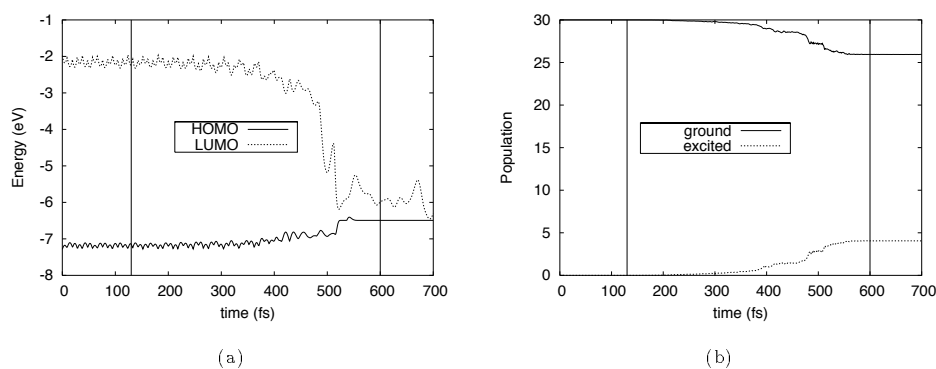
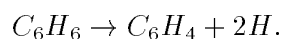


Figure 6. (a) HOMO-LUMO energy levels and (b) ground- and excited-state electron populations for a benzene molecule subjected to an 8.0 eV pulse with a duration of 470 fs and a fluence of 2.3 kJ/m².

Time (fs)	Bond	Type	Products
430	H12-C6	hydrogen expelled	$C_6H_5 + H$
431	H9-C2	hydrogen expelled	$C_6H_4 + 2H$
442	C3-C4	ring opened	$C_6H_4 + 2H$
454	C1-C6	carbon chain split	$2C_3H_2 + 2H$
455	C4-C5	CH expelled	$C_3H_2 + C_2H + CH + 2H$
455	C5-C10	hydrogen expelled	$C_3H_2 + C_2 + CH + 3H$
457	C3-H11	hydrogen expelled	$C_3H + C_2 + CH + 4H$
458	C4-C8	CH fragment broken	$C_3H + C_2 + C + 5H$
460	C2-C3	carbon expelled	$C_2H + C_2 + 2C + 5H$
465	C1-H7	hydrogen expelled	$2C_2 + 2C + 6H$
467	C1-C2	CC bond broken	$C_2 + 4C + 6H$
469	C5-C6	CC bond broken	$6C + 6H$

Table 5. Approximate times of events during dissociation of a benzene molecule subjected to an 8.0 eV laser pulse with a total duration of 470 fs and a fluence of 2.9 kJ/m².

atoms and exhibited ring opening, all during an interval of roughly 30 fs:



The hydrogen expulsion occurred shortly before the ring opening, as can be seen in Fig. 5.

The ultimate cause of this photochemical reaction is, of course, electronic ex-

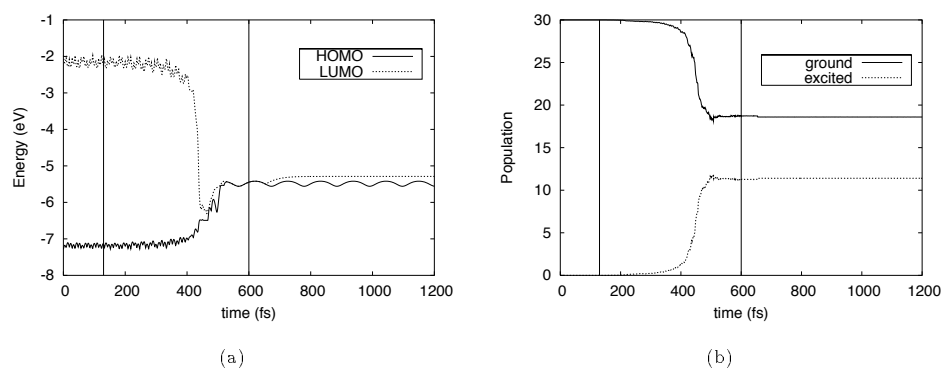
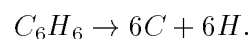


Figure 7. (a) HOMO-LUMO energy levels and (b) ground- and excited-state electron populations for a benzene molecule subjected to an 8.0 eV laser pulse with a total duration of 470 fs and a fluence of 2.9 kJ/m².

citation resulting from the laser pulse. About 170 fs into the pulse we observe both a rise in the number of electrons occupying excited states, as demonstrated by Fig. 6a, and a decrease in the width of the HOMO-LUMO energy gap, as shown by Fig. 6b. Just after the dissociation has occurred, the excited state population is about 13%.

At a much higher laser fluence of 2.9 kJ/m², the benzene ring completely dissociated into its constituent atoms:



The onset of dissociation occurred approximately 300 fs into the pulse excitation, and required roughly 40 fs for completion.

In Table 5, we list the approximate times at which various bond-breaking events occurred during this particular simulation. The details will vary, of course, but it is interesting to see that dissociation proceeds through specific molecular processes.

On a time scale similar to that associated with bond dissociation, we also observe a dramatic decrease in the HOMO-LUMO gap, as shown in Fig. 7a), with a very high population of excited-state electrons: roughly 38%, as can be seen in Fig. 7b).

In summary, we have used density-functional-based SERID to calculate the ground-state bondlengths, HOMO-LUMO gap, and vibrational frequencies for benzene, and the results are quite good in all cases, providing some confidence in the reliability of this technique. We have used the technique to examine the photodissociation of benzene over a range of intensities. Here we showed results for two representative cases: In the first, detachment of two hydrogen atoms is followed by ring opening. In the second, the fluence was so high that

the molecule is fully dissociated after a sequence of events exhibited in Table 5. These results illustrate the ability to monitor the motion of the nuclei and the related changes of electronic structure in microscopic detail.

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