Semiclassical electron-radiation-ion dynamics (SERID) and cis–trans photoisomerization of butadiene

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Abstract. Detailed simulations are reported for the dynamics of electrons and nuclei during the cis–trans isomerization of butadiene following a femtosecond-scale laser pulse. Our technique, semiclassical electron-radiation-ion dynamics (SERID), is fully described in the text. The one-electron Hamiltonian and ion–ion interactions employed in the present work are density-functional based. Following excitation of electrons by the laser pulse, all three C–C bonds in the butadiene molecule become longer, as electrons are promoted from the HOMO to both the LUMO and LUMO+1 levels. In the excited electronic state, the molecule rotates about all of its three C–C bonds. There are then non-adiabatic events near avoided crossings, with electronic transitions to the ground state via creation of vibrational excitations. The molecule continues to twist around the central bond and one of the terminal C–C bonds, until the trans-conformation is achieved. Various features in the behaviour of the vibrational modes can also be observed, including initial excitations due to the laser pulse, further excitations at avoided crossings and the redistribution of vibrational energy between modes.

1. Introduction

One of the most important unimolecular reactions of linear polyenes is photoinduced isomerization [1–3], which occurs in many important natural processes. For example, it is the primary event in rhodopsin responsible for vision [4, 5] and also has an important function in photosynthesis within bacteria [6]. It has therefore been the subject of many informative experimental [7–14] and theoretical [15–19] studies during the past few decades.

Three electronic states of the molecule are involved in the photoisomerization process in polyenes: the $1\,^1A_g$ ground state, the dipole allowed $1\,^1B_u$ state (obtained by $\text{HOMO} \rightarrow \text{LUMO}$), and the dipole forbidden $2\,^1A_g$ state (which can be obtained by a linear combination of the excitations $\text{HOMO-1} \rightarrow \text{LUMO}$, $\text{HOMO} \rightarrow \text{LUMO+1}$, and $\text{HOMO}^2 \rightarrow \text{LUMO}^2$). A generally accepted mechanism is that the polyene undergoes C–C torsional isomerization in the $1\,^1B_u$ state, following excitation of an electron, and then proceeds to the $2\,^1A_g$ state, following an internal conversion process. In this simple picture, the molecule passes to the ground state through a non-adiabatic transition, induced by coupling between the $2\,^1A_g$ and $1\,^1A_g$ states. The polyene then propagates within the ground state, ending
up in the *trans* or *cis* conformation. However, the actual photoisomerization process for polyenes is certainly more complex. It is still not fully understood, and continues to attract extensive new attention and research.

Experimental investigations mainly focus on a variety of spectroscopic techniques, including absorption, fluorescence, electron energy loss and resonance Raman spectroscopies, to probe the locations and the ordering of electronically excited states, and the non-adiabatic couplings between them [8, 9, 11–14]. Progress in the creation and employment of ultrashort laser pulses has led to numerous experimental studies of the dynamics during the photoisomerization process in polyenes. Significant achievements in this field include the results that (i) 11-\textit{cis} to all-\textit{trans} torsional isomerization of retinal in rhodopsin is found from differential absorption spectra to be essentially completed in only 200 fs [7] and (ii) \textit{trans} → \textit{cis} isomerization of butadiene is found, in a recent non-resonant multiphoton ionization experiment, to proceed within about 420 fs [10].

Many theoretical investigations attempt to provide detailed potential energy surfaces for the ground state and electronically excited states, which can then be used to understand the isomerization reaction path. Semiclassical molecular dynamics simulations have also been used by a number of groups to study photoisomerization in polyenes [20–26]. Krawczyk et al. used a vibronic-coupling approach to investigate the non-adiabatic coupling between two low-lying electronically excited states, $1^1B_u$ and $2^1A_g$, in the vicinity of the equilibrium geometry for the electronic ground state [22]. Their study was limited to the most relevant active vibrational modes. Ito and Ohmine employed a parametrized model Hamiltonian and surface-hopping scheme to study the dynamics of \textit{trans}-butadiene photoisomerization [23]. The modified Hamiltonian in their work is a function of a limited set of atomic degrees of freedom, including C–C bond stretching, bond bending and torsional modes. Robb and co-workers utilized valence-bond theory, combined with a molecular-mechanics force field, to investigate the electronic excited-state dynamics of \textit{trans}-butadiene [24] and other polyenes with longer chains [25]. For a detailed understanding of the dynamics of photoisomerization, it is advantageous to calculate the forces on the nuclei for all the internal coordinates of the molecule, and at every time step, as the molecule propagates from reactant to product. To our knowledge, this kind of calculation has only been applied in studies of the \textit{cis} → \textit{trans} photoisomerization process in ethylene, by Ben-Nun and Martínez [26].

In previous work, the initial electronic configuration in semiclassical molecular dynamics calculations has always been prepared by artificially promoting a single electron from the ground state to an excited state. However, this is a highly unphysical representation of the true excitation due to a laser pulse. The electronic configuration of a reactant generated by an actual laser pulse is one in which the different excited states are populated with various amplitudes, depending not only on the electronic properties of the reactant but also on the properties of the laser pulse, including the wavelength, fluence and duration [27]. A realistic simulation of photoisomerization should therefore begin with laser excitation, with a laser pulse similar to those used in the experiments.

A realistic method for investigating the response of molecules to ultrashort laser irradiation has been developed by our group [28]. We call the general method semiclassical electron-radiation-ion dynamics (SERID) in order to emphasize both its strengths and its limitations. The valence electrons are treated
quantum-mechanically, but both the radiation field and the motion of the ion cores are treated classically. (This is not as severe a limitation as it may first appear to be, because a semiclassical treatment in time-dependent perturbation theory still gives effective \( n \)-photon and \( n \)-phonon processes in absorption and stimulated emission.) In the version of the method used here, electron correlations are neglected and the one-electron Hamiltonian \( H \) has a semi-empirical form, but the values of the parameters determining both \( H \) and the ion–ion repulsion were determined in the density-functional calculations of Frauenheim and co-workers [29]. These parameters were found to give a remarkably good description of \( \text{C}_{60} \) responding to laser pulses of various intensities, ranging from low to very high [30]. The description of the C–H bond is also quite accurate, so it is clear that this model is quite suitable for butadiene, the subject of the present paper.

Our method is designed to treat the forces on the atomic nuclei (or ion cores) when there are multiple electronic excitations, with the electronic wavefunctions updated at every time step via solution of the time-dependent Schrödinger equation. The time-dependent vector potential for the radiation field is included in the electronic Hamiltonian, allowing a proper treatment of the laser excitation process. This model has also proved to have great potential for simulating quantum control of chemical reactions [31].

1,3-butadiene (hereafter called simply butadiene) can be considered a model compound for studying the photoisomerization of polyenes, since its small size permits a meaningful comparison of theory and experiment. Photoisomerization can start from either the \( \text{cis} \) or the \( \text{trans} \) conformation. In the present paper, we present results for \( \text{cis}\rightarrow \text{trans} \). We will first give a description of our method, and then present the results together with a detailed discussion. A summary is given at the end.

2. Description of the method

Our technique is based on simple principles. The electron dynamics is determined by the time-dependent Schrödinger equation in a non-orthogonal basis

\[
\frac{i\hbar}{\partial t} \Psi_j = S^{-1} \cdot H \cdot \Psi_j, \quad (1)
\]

the motion of the nuclei (or ion cores) by Ehrenfest’s theorem

\[
M_\ell \frac{d^2 X_{\ell\alpha}}{dt^2} = -\frac{1}{2} \sum_j \Psi_j^\dagger \cdot \left( \frac{\partial H}{\partial X_{\ell\alpha}} - i\hbar \frac{\partial S}{\partial X_{\ell\alpha}} \frac{\partial}{\partial t} \right) \cdot \Psi_j + h.c. - \frac{\partial U_{\text{rep}}}{\partial X_{\ell\alpha}}, \quad (2)
\]

and the coupling of the electrons to the radiation field by the time-dependent Peierls substitution

\[
H_{ab}(X - \dot{X}) = H_{ab}^0(X - \dot{X}) \exp \left( \frac{iq}{\hbar c} A(t) \cdot (X - \dot{X}) \right), \quad (3)
\]

where \( S \) is the overlap matrix for the atomic orbitals, \( X_{\ell\alpha} \) is an ion coordinate, \( A(t) \) is the vector potential for the radiation field and the rest of the notation is explained below.

To put our technique in perspective, let us now list the various approximations upon which it is currently based, together with an indication of when these
approximations may be significant, how they may be relaxed in the future, and their validity in the present context.

**Approximation 1. The atomic nuclei are treated as positive point charges.**

(a) Potential problems: the finite sizes and internal structure of the nuclei are essentially irrelevant for the phenomena considered in an ordinary chemical context, but the hyperfine interaction can be observable. Also, as is well known in the treatment of ortho- and para-hydrogen, symmetry implies a connection between the nuclear spin and rotational states of the molecule.

(b) Potential extensions: it is not difficult to add nuclear spin effects when they have any significance.

(c) Relevance in the present context: nuclear spin is unimportant for the photochemical reactions considered here.

**Approximation 2. The treatment is non-relativistic.**

(a) Potential problems: the inner core electrons are relativistic in heavy atoms. Even the valence electrons have tails extending into the region near the nucleus, so their energies will be slightly perturbed by relativistic effects in the case of heavy atoms.

(c) Potential extensions: the full machinery of relativistic field theory will never be required for the class of problems envisioned here. Any relativistic corrections can be handled with the Dirac equation (which only makes the method more complicated) or with the leading relativistic corrections obtained in the Foldy–Wouthuysen reduction.

(d) Relevance in the present context: relativity is unimportant for the problems envisioned here.

**Approximation 3. The nuclear motion is treated classically.**

(a) Potential problems: the zero-point energy can be a significant part of the total energy for a molecule with light nuclei, like H$_2$. In addition, there is a more subtle problem when the nuclear wavefunction can evolve along multiple paths. Let $M$ and $X$ be any nuclear mass and coordinate, and let $P$ be the momentum conjugate to $X$. The Heisenberg equations of motion for the corresponding operators $\hat{X}$ and $\hat{P}$ simplify to $d\hat{X}/dt = \hat{P}/M$ and $d\hat{P}/dt = -\partial\hat{H}/\partial\hat{X}$, where $\hat{H}$ is the Hamiltonian for the complete system. It follows that $Md^2\hat{X}/dt^2 = -\partial\hat{H}/\partial\hat{X}$, and so one obtains Ehrenfest’s theorem [32]

$$M \frac{d^2\langle \hat{X} \rangle}{dt^2} = -\left\langle \frac{\partial\hat{H}}{\partial\hat{X}} \right\rangle.$$  \hspace{1cm} (4)

In a classical treatment, the nuclei are regarded as very massive and the wavefunction for nuclear motion highly localized about each average position $\langle \hat{X} \rangle$, so that $\hat{X}$ can be replaced by a classical coordinate $X$. This is an approximation, of course, and it will fail in those situations where the uncertainty in nuclear positions has a significant influence on the outcome. For example, suppose that a diatomic molecule is subjected to a laser pulse
that promotes electrons from bonding to antibonding states. This raises the effective potential energy $V(r)$ associated with the relative coordinate $r$. If $V(r)$ becomes strongly repulsive for a long period of time, the molecule will dissociate with high probability and quantum effects will not have a significant effect on the outcome. Also, if $V(r)$ remains strongly attractive, there will be a low probability of dissociation, and the outcome will again not be significantly influenced by quantum effects. On the other hand, if $V(r)$ is such that the molecule is very near the threshold for dissociation, then the evolution of the wavefunction for nuclear motion will produce two branches, corresponding to dissociation and no dissociation. This is precisely analogous to similar phenomena in elementary quantum mechanics, where the wavefunction of a particle incident on a barrier has amplitudes for both transmission and reflection, or the cat in Schrödinger’s famous thought experiment has amplitudes for being both alive and dead.

(b) Potential extensions: for very simple systems, a quantum treatment of the nuclear motion is feasible, either by direct solution of the time-dependent Schrödinger equation or by some variation of Bohm’s formulation of quantum mechanics [33, 34], in which

$$M \frac{d^2 X_p}{dt^2} = -\frac{\partial U}{\partial X}, U = V + V_Q,$$

for a one-dimensional problem. Here $V$ is the actual potential, $V_Q$ is Bohm’s quantum potential and $X_p$ is defined by

$$\int_{X_{p(t)}}^{\infty} \rho(X,t) \, dX = P,$$

where $\rho(X,t)$ is the probability density and $P$ is any chosen probability between 0 and 1.

(c) Relevance in the present context: a rough measure of the importance of quantum effects is provided by $\Delta E \Delta t \sim \hbar$, with $\Delta t \sim 100$ fs or more for the nuclei, so that $\Delta E \sim 0.01$ eV. When two outcomes are separated by $\sim 0.01$ eV, therefore, one expects that both may occur with comparable amplitudes, and that a classical treatment is not sufficient in this case. For the simulations reported here, however, the energy scales are typically two orders of magnitudes larger. (For example, see figure 14 in section 3.) Alternatively, one might use the amplitude of the zero-point vibrations as a measure of the importance of quantum effects. In an Einstein model for the vibrations of a C atom, a rough estimate is $\langle (\Delta X^2)^2 \rangle^{1/2} \sim (\hbar/(M \omega_0))^{1/2} \sim 0.1 \, \text{Å}$, so the quantum motion of the principal atoms in an organic molecule is rather small under normal circumstances.

For these reasons, one expects that it is a quite good approximation to treat the nuclear motion classically in simulations like those of the present paper, where one is not concerned with subtleties like behaviour very near threshold or other regimes where quantum effects are amplified.
Approximation 4. The radiation field is treated classically.

(a) Potential problems: with a classical treatment of the radiation field, there is no spontaneous emission.

(b) Potential extensions: if it were necessary, one might add random fluctuations of the radiation field to mimic the vacuum fluctuations that induce spontaneous emission.

(c) Relevance in the present context: spontaneous emission, like other vacuum effects, is relatively weak and does not have a large effect on the times scales of interest in the present paper.

The present method treats both the nuclear motion and the electromagnetic field classically, so it is consistently a semiclassical method. Semiclassical treatments have the pleasant feature that they effectively include both $n$-photon and $n$-phonon processes. (Here we broaden the term ‘phonon’ to include vibrational quanta in a molecule.) That is, first-order time-dependent perturbation theory implies that the electrons gain or lose an energy $\hbar \omega$ during absorption or stimulated emission, and $n$th-order perturbation theory implies that the change in energy is $\pm n\hbar \omega$. Here $\hbar \omega$ is either a photon or phonon energy, and there is a distribution of frequencies $\omega$ in both the laser pulse and the molecular vibrations.

Approximation 5. The electrons are treated in a time-dependent mean-field picture, with many-body effects neglected.

(a) Potential problems: this is probably the most severe limitation of the method as it is currently formulated. It will eventually be necessary to extend the method by including some electron–electron correlation effects, in order to address a broader range of problems. Some examples of the importance of many-body effects are the following. (i) In either a molecule or an insulator, one-electron descriptions give HOMO–LUMO gaps that are typically too small. (ii) An admixture of two or more electronic configurations may be required to give the proper ordering of electronic energy levels in a molecule. (iii) In a semiconductor, electron–electron collisions lead to rapid equilibration of carriers (i.e. electrons promoted to the conduction band by laser excitation). (iv) Excitons, with electron and hole bound by the Coulomb attraction, are important for energy transport in many organic and biological systems.

(b) Potential extensions: in physics, many-body effects are frequently addressed with techniques involving Green’s functions and self-energies. From this point of view, a proper treatment of non-equilibrium problems requires techniques like those introduced by Martin and Schwinger [35], Kadanoff and Baym [36] or Keldysh [37], which involve self-energies that are still more complicated than those encountered for systems in equilibrium. In chemistry, many-body effects are conventionally described by configuration interaction. One can imagine extending the present method via either approach, either by using a model self-energy or by including a small number of additional configurations. (There are, of course, a variety of other approaches that may be useful [38].) The method then becomes more complicated, but also more quantitative and broadly applicable.
(c) Relevance in the present context: in the immediate context we are interested in the basic processes that occur during photoisomerization. Since our description of the excited states derives from density-functional theory, it is not precisely correct. In fact, for butadiene the density-functional HOMO–LUMO gap of 4.2 eV is about 2/3 of the measured gap, and we have scaled down the photon energy for the laser pulse accordingly. However, density-functional theory yields good results for the bonding, so the dynamics of the photoisomerization process following the laser pulse is reliable.

Approximation 6. Only the valence electrons are treated, with the inner electrons plus nucleus represented as an inert core.

(a) Potential problems: high energy processes can lead to core excitations. Core polarization can also have significant effects.
(b) Potential extensions: inclusion of the core electrons merely leads to a larger computational problem.
(c) Relevance in the present context: the core electrons can be effectively replaced by a pseudopotential when one is concerned with chemical bonding and excitations of the order of a few electronvolts.

Approximation 7. The basis functions are atomic orbitals.

(a) Potential problems: in practice, only a finite basis is used, with a correspondingly limited set of excited states. For example, the excited d states can be important even for atoms which have only s and p valence electrons. These d states hybridize with the s and p states, and tend to push the s and p excited states to lower energies through level repulsion. Also, of course, excitation to the d states themselves can be important. Furthermore, even if all the atomic orbitals could be included, the ionized states would still be missing, and ionization plays a critical role in many photochemical reactions. Finally, there is a more subtle effect associated with the fact that the basis functions are moving with the atoms: if a one-electron wavefunction $\Psi_j$ is written in the form

$$\Psi_j(x, t) = \sum_{\ell a} \Psi_j(\ell a, t) \phi_a(x - X_\ell),$$

where $\phi_a(x - X_\ell)$ is an atomic orbital on site $X_\ell$, then $\partial \Psi_j(x, t)/\partial t$ contains a contribution involving $X_\ell \cdot (\partial \phi_a(x - X_\ell)/\partial x)$, due to motion of the atomic orbital, in addition to the usual contribution involving $\partial \Psi_j(\ell a, t)/\partial t$.

(b) Potential extensions: by simply adding more atomic orbitals, one obtains a more complete description of the excited states. Ionization can be treated by either including the true ionized states or by modelling them as free-electron states. A numerically efficient method for treating ionization will be given elsewhere, where we will also present an approximate procedure for including $\mathbf{X} (\partial \phi_a(x - \mathbf{X})/\partial \mathbf{X})$ in the solution of the time-dependent Schrödinger equation.

(c) Relevance in the present context: in the immediate context of photoisomerization with a photon energy which just matches the HOMO–LUMO gap,
it is a reasonable approximation to neglect the higher excited states and ionization. Also, we have carried out test calculations with our method for including the term with $\partial \psi_0(\mathbf{x} - \mathbf{X})/\partial \mathbf{X}$, and, in work that will be presented elsewhere, we find that it is a good approximation to neglect this term.

**Approximation 8.** The spin–orbit interaction, exchange interaction and other spin-dependent interactions are neglected.

(a) Potential problems: the spin–orbit interaction is a fundamental part of the one-electron Hamiltonian, which follows from the Dirac equation and which is already important in the ground state of a free atom. In a molecule it can induce spin flips, or singlet-to-triplet and triplet-to-singlet transitions. The exchange interaction is an important consequence of the Pauli principle, which accounts for the electronic structure of transition metal and rare earth atoms, and for the magnetism of systems containing these atoms. The interaction of an electron with an external magnetic field is also spin dependent.

(b) Potential extensions: by doubling the size of the basis set, one can include all of these spin-dependent interactions, at least with approximate or empirical models.

(c) Relevance in the present context: spin-dependent interactions have only a weak effect for the specific problem addressed in the present paper.

**Approximation 9.** The calculations are not explicitly self-consistent, and there is no explicit Coulomb repulsion.

(a) Potential problems: during both bonding and excitation, the electronic charge is redistributed. Coulomb repulsion after charge redistribution plays an important role in determining even the geometry. There are important processes, such as charge-transfer reactions, in which Coulomb interactions play a central role.

(b) Potential extensions: one can model these effects with simple extensions of the present approach, via the use of a Löwdin population analysis to determine the charge, the use of a Hubbard $U$ to shift the on-site Hamiltonian matrix elements, and explicit Coulomb interactions for ionic systems.

(c) Relevance in the present context: the main effects of self-consistency and Coulomb repulsion are implicitly included in the present model, because the parameters are determined in density-functional calculations.

**Approximation 10.** The Hamiltonian matrix elements and core–core repulsion are determined from calculations involving pairs of atoms.

(a) Potential problems: the exact Hamiltonian matrix is determined globally, by the whole system, rather than locally, by the bonding of pairs of atoms.

(b) Potential extensions: one might add environmental effects in the determination of the Hamiltonian matrix and repulsive interaction.

(c) Relevance in the present context: one expects the pairwise interactions to be of dominant importance, and for $C_{60}$ the present model has proved to
give a good description of bonding, vibrational frequencies, response to a laser pulse and dissociation [30].

**Approximation 11. The Peierls substitution is used to couple the electrons to the radiation field.**

(a) Potential problems: the Peierls substitution does not yield intra-atomic excitations, since it involves $R - R'$ for two different sites. Also, in the case of low-frequency radiation, the ion cores should be coupled to the field.

(b) Potential extensions: if intra-atomic excitations are of interest, one can add a term to the Hamiltonian containing the atomic dipole moment. Regarding the direct interaction with the ion cores, it is trivial to couple these to the radiation field via a force term $qE$.

(c) Relevance in the present context: the main features of the interaction of a molecule with a laser pulse are included through the Peierls substitution. It is the behaviour of the molecule after application of the laser pulse that must be treated with more care. Also, for photon energies of order 2 eV, the period of oscillation is of order 2 fs. The radiation field then oscillates with a frequency that is two orders of magnitude too fast for the ion cores to show an appreciable response.

**Approximation 12. The influence of a larger environment is not included.**

(a) Potential problems: much of chemistry and biology involves an environment. As one example, we mention the chromopore retinal within the protein rhodopsin, which itself lies within the cone cell of an eye. A simpler example is a molecule in a fluid.

(b) Potential extensions: the most important effects of the environment can often be modelled with a combination of molecular mechanics and electrostatic fields.

(c) Relevance in the present context: here we are considering a free molecule on a time scale too short for collisions.

Now we are in a position to describe our approach in more detail. We begin with a semiclassical action

$$ S = \int \! dt L, $$

$$ L = \frac{1}{2} \langle \Psi_e | \left( i \hbar \frac{\partial}{\partial t} - \mathcal{H}_e \right) | \Psi_e \rangle + \text{h.c.} + \frac{1}{2} \sum_{\ell \alpha} M_{\ell \alpha} \left( \frac{dX_{\ell \alpha}}{dt} \right)^2 - U_{ii}, $$

$$ \mathcal{H}_e = \sum_j H_e(x_j), \quad H_e(x) = T + v_{ii}(x) + \epsilon_{ee}(x). $$

Here $j$ labels a valence electron, $\ell$ labels an ion core, $\alpha = x, y, z$, ‘h.c.’ represents the Hermitian conjugate of the first term in (9) and $T$ is the kinetic energy operator. Also, $U_{ii}$ is a potential energy representing the repulsive interaction between ion cores, so it is a function of their coordinates $X_{i\alpha}$. The electron–ion interaction $v_{ii}(x)$ also depends on the ion positions $X_{i\alpha}$, and it may be given by a non-local pseudopotential. The contribution $\epsilon_{ee}(x)$ is due to electron–electron interactions, and it is a functional of $|\Psi_e\rangle$ or the one-electron wavefunctions.
\( \Psi_j(x, t) \) defined below. We will see that the present approach is equivalent to more usual time-dependent Hartree-like treatments in which the Hamiltonian is written in the form

\[
H_0 = \sum_j H_1(x_j) + \frac{1}{2} \sum_{jj'} H_2(x_j, x_{j'}). \tag{11}
\]

We assume that the core electrons in an atom move rigidly with the nucleus, so that an ion core can be treated essentially as an extended nucleus with charge \( Z e \).

We now adopt a time-dependent self-consistent field picture, in which \( \Psi_e \) is approximated by an antisymmetrized and normalized product of one-electron states. The wavefunction in the coordinate representation is then written as

\[
\Psi_e(x_1, x_2, \ldots, t) = A \prod_j \Psi_j(x_j, t). \tag{12}
\]

Since

\[
\langle \Psi_j | \Psi_j \rangle = \int d^3x \Psi_j^\dagger(x_j, t) \Psi_j(x_j, t) = \delta_{jj'},
\]

it follows that

\[
\left\langle \Psi_e \right| \left( i \hbar \frac{\partial}{\partial t} - \mathcal{H}_e \right) \left| \Psi_e \right\rangle = \sum_j \int d^3x \Psi_j^\dagger(x) \left[ i \hbar \frac{\partial}{\partial t} - H_e(x) \right] \Psi_j(x). \tag{14}
\]

The one-electron wavefunctions \( \Psi_j \) are represented by a set of localized basis functions \( \phi_{\ell a}(x) \):

\[
\Psi_j(x, t) = \sum_{\ell a} \Psi_j(\ell a, t) \phi_{\ell a}(x) \tag{15}
\]

with

\[
\int d^3x \phi_{\ell a}^\dagger(x) \phi_{\ell' a'}(x) = S(\ell a, \ell' a'), \tag{16}
\]

\[
\int d^3x \phi_{\ell a}^\dagger(x) H_e \phi_{\ell' a'}(x) = H_e(\ell a, \ell' a'). \tag{17}
\]

Let \( \Psi_j \) be the vector with components \( \Psi_j(\ell a) \) and let \( H_e \) be the matrix with elements \( H_e(\ell a, \ell' a') \). The basis functions \( \phi_{\ell a}(x) \) move with the ion cores, so the \( H_e(\ell a, \ell' a') \) are functions of the \( X_{\ell a} \).

Substitution of (15) into (9) then gives

\[
L = \frac{1}{2} \sum_j \Psi_j^\dagger \left( i \hbar S \frac{\partial}{\partial t} - H_e \right) \Psi_j + \text{h.c.} + \frac{1}{2} \sum_{\ell a} M_{\ell} \left( \frac{dX_{\ell a}}{dt} \right)^2 U_{ii}. \tag{18}
\]

(As mentioned in the discussion of Approximation 7, the time variation of \( \phi_{\ell a} \) and \( S \) is neglected in the present paper.) The overlap matrix \( S \), the ion–ion interaction \( U_{ii} \) and \( H_e \) all depend on the atomic coordinates \( X_{\ell a} \). When there is an electromagnetic field present, \( H_e \) will also have an explicit dependence on the time \( t \).

As usual, the equations of motion are determined by extremalizing the action with respect to variations \( \delta \Psi_j^\dagger \) and \( \delta X_{\ell a} \) (after performing an integration by parts in (8)). The result is a one-electron Schrödinger equation

\[
i \hbar \frac{\partial \Psi_j}{\partial t} = S^{-1} \cdot H \cdot \Psi_j \tag{19}
\]
or
\[ -i\hbar \frac{\partial \Psi_j^\dagger}{\partial t} = \Psi_j^\dagger \cdot H \cdot S^{-1} \] (20)

Together with a Newton’s equation for the atoms:
\[ M \frac{d^2 X_{\ell a}}{dt^2} = -\frac{1}{2} \sum_j \Psi_j^\dagger \cdot \left( \frac{\partial H}{\partial X_{\ell a}} - i\hbar \frac{\partial S}{\partial X_{\ell a} \partial t} \right) \cdot \Psi_j + h.c. - \frac{\partial U_{\text{rep}}}{\partial X_{\ell a}} \] (21)
\[ = -\sum_j \Psi_j^\dagger \cdot \left( \frac{\partial H}{\partial X_{\ell a}} - \frac{1}{2} \frac{\partial S}{\partial X_{\ell a}} \cdot S^{-1} \cdot H - \frac{1}{2} \frac{\partial S}{\partial X_{\ell a}} \cdot S \cdot \frac{\partial S}{\partial X_{\ell a}} \right) \cdot \Psi_j - \frac{\partial U_{\text{rep}}}{\partial X_{\ell a}}, \] (22)

where
\[ H \cdot \Psi_j = H_e \cdot \Psi_j + \sum_j \Psi_j^\dagger \cdot \left( \frac{\delta H_e}{\delta \Psi_j} \right) \cdot \Psi_j, \] (23)
\[ U_{\text{rep}} = U_{ii} - U_{ee}, \] (24)
\[ U_{ee} = \sum_j \Psi_j^\dagger \cdot \sum_j \Psi_j^\dagger \cdot \left( \frac{\delta H_e}{\delta \Psi_j^\dagger} \right) \cdot \Psi_j \] (25)

with
\[ \Psi_j^\dagger \cdot \sum_j \left[ \Psi_j^\dagger \cdot \left( \frac{\delta H_e}{\delta \Psi_j^\dagger} \right) \cdot \Psi_j \right] = \sum_{\ell a} \Psi_j^\dagger(\ell a) \sum_j \left[ \Psi_j^\dagger \cdot \left( \frac{\delta H_e}{\delta \Psi_j^\dagger(\ell a)} \right) \cdot \Psi_j \right] \] (26)

since the \( \Psi_j \) and \( X_{\ell a} \) vary independently in \( H_e \). Let
\[ H' = \sum_j \sum_j \left[ \Psi_j^\dagger \cdot \left( \frac{\delta H_e}{\delta \Psi_j^\dagger} \right) \cdot \Psi_j \right] \Psi_j^\dagger \cdot S. \] (27)

Then (23) follows from
\[ H = H_e + H' \] (28)

since
\[ \Psi_j^\dagger \cdot S \cdot \Psi_j = \int d^3x \Psi_j^\dagger(x, t) \Psi_j(x, t) = \delta_{jj}. \] (29)

If the Pauli principle is satisfied at time \( t = 0 \), it will continue to hold at later times:
\[ i\hbar \frac{\partial}{\partial t} \left( \Psi_j^\dagger \cdot S \cdot \Psi_j \right) = \Psi_j^\dagger \cdot S \cdot (S^{-1} \cdot H \cdot \Psi_j) \]
\[ - \left( \Psi_j^\dagger \cdot H \cdot S^{-1} \right) \cdot S \cdot \Psi_j \] (30)
\[ = 0. \] (31)

For example, if an excited state becomes 50% occupied by one electron, then it is 50% blocked to all the other electrons.
For a better understanding of the above equations, let us temporarily revert to the coordinate representation and use forms which correspond to those of time-dependent density-functional theory in the local-density approximation [39]:

\[ \varepsilon_{ee}(\mathbf{x}) = \frac{1}{2} v_e(\mathbf{x}) + \varepsilon_{xc}(\mathbf{x}), \]

\[ v_e(\mathbf{x}) = \int d^3x' \frac{e^2 \rho(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|}, \]

\[ \rho(\mathbf{x}) = \sum_j \Psi_j^\dagger(\mathbf{x}) \Psi_j(\mathbf{x}), \]

where \( \varepsilon_{xc}(\mathbf{x}) \) is a parametrized function of the local density \( \rho(\mathbf{x}) \). In this case we have

\[ \frac{\delta H_e(\mathbf{x}')}{\delta \Psi_j^\dagger(\mathbf{x})} = \frac{\delta \varepsilon_{ee}(\mathbf{x}')}{\delta \Psi_j^\dagger(\mathbf{x})} \]

\[ = \frac{1}{2} \frac{e^2}{|\mathbf{x}' - \mathbf{x}|} \Psi_j(\mathbf{x}) + \beta(\mathbf{x}) \varepsilon_{xc}(\mathbf{x}') \rho(\mathbf{x})^{-1} \delta(\mathbf{x}' - \mathbf{x}) \Psi_j(\mathbf{x}), \]

where

\[ \beta(\mathbf{x}) \equiv \frac{[d \log \varepsilon_{xc}(\rho)/d \log \rho]_{\rho = \rho(\mathbf{x})}}{1} , \]

so that

\[ \int d^3x' \sum_j \Psi_j^\dagger(\mathbf{x}') \left( \frac{\delta H_e(\mathbf{x}')}{\delta \Psi_j^\dagger(\mathbf{x})} \right) \Psi_j(\mathbf{x}) = \frac{1}{2} \int d^3x' \frac{e^2 \rho(\mathbf{x}')}{|\mathbf{x}' - \mathbf{x}|} \Psi_j(\mathbf{x}) + \beta(\mathbf{x}) \varepsilon_{xc}(\mathbf{x}) \Psi_j(\mathbf{x}). \]

(For example, the crudest approximation is to neglect correlation and take \( \varepsilon_{xc} \propto \rho^{1/3} \), in which case \( \beta = 1/3 \).) From the above equations we then have

\[ H = H_e + \frac{1}{2} v_e(\mathbf{x}) + \beta(\mathbf{x}) \varepsilon_{xc}(\mathbf{x}), \]

\[ U_{\text{rep}} = U_{ii} - \int d^3x \left[ \frac{1}{2} v_e(\mathbf{x}) + \beta(\mathbf{x}) \varepsilon_{xc}(\mathbf{x}) \right] \rho(\mathbf{x}) \]

\[ = U_{ii} - U_{ee}, \]

where

\[ U_{ii} = \sum_{\ell > \ell'} \frac{Z_{\ell} Z_{\ell'} e^2}{|\mathbf{r}_{\ell} - \mathbf{r}_{\ell'}|} \]

\[ U_{ee} = U_{\text{Coul}} + U_{xc}, \]

\[ U_{\text{Coul}} = \frac{1}{2} \int d^3x' \int d^3x' \frac{e^2 \rho(\mathbf{x}) \rho(\mathbf{x}')}{|\mathbf{x}' - \mathbf{x}|}, \]

\[ U_{xc} = \int d^3x \beta(\mathbf{x}) \varepsilon_{xc}(\mathbf{x}) \rho(\mathbf{x}) \]

with \( \varepsilon_{xc} < 0 \).

If it is viewed as an effective potential energy, \( U_{\text{rep}} \) corresponds to repulsive forces between the ion cores. The electronic charge is more distributed than the ionic charge, so the Coulomb repulsion between ion cores is not fully screened as it
would be for neutral atoms. Also, the strength of the electron–electron repulsion is
reduced by exchange and correlation effects, since each electron is surrounded by
an exchange-and-correlation hole.

In a density-functional treatment, (19) and (22) become

\[ i\hbar \frac{\partial \Psi_j}{\partial t} = H\Psi_j, \]
\[ M \frac{d^2 X_{i\alpha}}{dt^2} = -\sum_j d^3 x \Psi_j^\dagger \left( \frac{\partial H}{\partial X_{i\alpha}} \right) \Psi_j - \frac{\partial U_{\text{rep}}}{\partial X_{i\alpha}}. \]

These two equations, together with

\[ T = \frac{1}{2m} \left( -i\hbar \nabla - \frac{q}{c} A \right)^2, \]

where \( q \) is the charge of the electron, represent a first-principles, density-
functional version of the present approach.

Equations (19) and (22) represent the non-orthogonal formulation of our
method. These same equations can, however, be cast into an orthogonalized
form if we write the Lagrangian (18) as

\[ L = \frac{1}{2} \sum_j \Psi_j^\dagger \left( i\hbar \frac{\partial}{\partial t} - \frac{q}{c} A \right) \Psi_j + h.c. + \frac{1}{2} \sum_{i\alpha} M \left( \frac{d X_{i\alpha}}{dt} \right)^2 - U_{\text{ii}}, \]

where

\[ \Psi = S^{1/2}_j \Psi, \quad \overline{H}_e = S^{-1/2}_e H_e S^{-1/2}. \]

Repetition of the arguments above then leads to

\[ i\hbar \frac{\partial \overline{\Psi}_j}{\partial t} = \overline{H} \cdot \overline{\Psi}_j, \]
\[ M \frac{d^2 X_{i\alpha}}{dt^2} = -\sum_j \overline{\Psi}_j^\dagger \frac{\partial \overline{H}}{\partial X_{i\alpha}} \overline{\Psi}_j - \frac{\partial \overline{U_{\text{rep}}}}{\partial X_{i\alpha}}. \]

In a semi-empirical or density-functional-based tight-binding scheme, one can fit
either \( \overline{H} \) and \( \overline{U_{\text{rep}}} \) or \( H \) and \( U_{\text{rep}} \) to experiment and pre-existing theoretical
calculations.

In the following we will use the notation \( H \) and \( \Psi_j \) for both the orthogonal and
non-orthogonal calculations, and the context will establish which is being used.
For the orthogonal case, then, the equations of motion are

\[ i\hbar \frac{\partial \Psi_j}{\partial t} = H(t) \Psi_j, \]
\[ M \ddot{X} = -\sum_j \Psi_j^\dagger \frac{\partial H}{\partial X} \cdot \Psi_j - \frac{\partial U_{\text{rep}}}{\partial X}. \]

where \( M \) is the mass and \( X \) is the coordinate of any ion. These are respectively
the time-dependent Schrödinger equation and Ehrenfest’s theorem.

The electrons and ions are coupled in (53) and (54), because \( H \) is a function of
the ion coordinates and the forces on the ions are influenced by the electronic
states. We now need to couple the electrons to the radiation field. (One can also
easily couple the ions to the electromagnetic field, but this is a minor effect if the
field oscillates on a one femtosecond time scale, two orders of magnitude smaller
than the response time of the ions.) The most convenient way to introduce the field
into the electronic Hamiltonian is to employ a time-dependent Peierls substitution. First consider the standard Hamiltonian in the coordinate representation with a time-dependent electromagnetic vector potential $A$:

$$H = (\frac{\mathbf{p}}{\hbar} - \frac{q}{c} \mathbf{A})^2/2m + V(\mathbf{x}),$$

(55)

where $\mathbf{p} = -i\hbar \nabla$. This is equivalent to

$$H = \exp\left(\frac{i\mathbf{q}}{\hbar c} \mathbf{A} \cdot \mathbf{d}x\right) H^0 \exp\left(-\frac{i\mathbf{q}}{\hbar c} \mathbf{A} \cdot \mathbf{d}x\right)$$

(56)

with

$$H^0 = \frac{\mathbf{p}^2}{2m} + V(\mathbf{x})$$

(57)

as one can easily verify by substituting (57) into (56) and letting $H$ operate on an arbitrary function $\Psi(\mathbf{x})$. To employ (56) in a localized basis, we recognize that the matrix elements of (56) are the same as the matrix elements of (57) with the localized basis functions $\phi_a(\mathbf{x} - \mathbf{X})$ multiplied by exp ($-i\mathbf{q} \mathbf{A} \cdot \mathbf{d}x/\hbar c$). When treating excitations in a molecule it is a reasonable approximation to take $\mathbf{A} \cdot \mathbf{d}x \approx \mathbf{A} \cdot \mathbf{x} \approx \mathbf{A} \cdot \mathbf{X}$, provided that $\mathbf{A}$ is slowly-varying on an atomic scale (as it is for electromagnetic radiation with $\hbar \omega \sim 10$eV or less) and that the basis functions can be regarded as well localized on atomic sites. Then the matrix elements $H_{ab}(\mathbf{X} - \mathbf{X'})$ are modified by the Peierls substitution

$$H_{ab}(\mathbf{X} - \mathbf{X'}) = H^0_{ab}(\mathbf{X} - \mathbf{X'}) \exp\left(\frac{i\mathbf{q}}{\hbar c} \mathbf{A} \cdot (\mathbf{X} - \mathbf{X}')\right).$$

(58)

This approach requires no additional parameters and in principle is valid for arbitrarily strong time-dependent fields (except, as mentioned above, ionization requires an extension in which the ionized states are included).

Solution of the nuclear equations of motion (54) is essentially the same as in ordinary molecular dynamics, and the velocity Verlet method appears to be optimal. Solution of (53) requires more care, since a naive algorithm for this first-order equation fails to conserve probability. In earlier work we followed a standard prescription and wrote the time-evolution equation in the form

$$\exp\left(\frac{i\mathbf{H} \Delta t}{2\hbar}\right) \cdot \Psi_j(t + \Delta t) = \exp\left(-\frac{i\mathbf{H} \Delta t}{2\hbar}\right) \cdot \Psi_j(t).$$

(59)

If the exponential is approximated by its first two terms, this gives the Cayley algorithm

$$\Psi_j(t + \Delta t) = \left(1 + \frac{i\mathbf{H} \Delta t}{2\hbar}\right)^{-1} \cdot \left(1 - \frac{i\mathbf{H} \Delta t}{2\hbar}\right) \cdot \Psi_j(t).$$

(60)

Then probability and orthogonality are preserved because

$$\Psi_j^\dagger(t + \Delta t) \cdot \Psi_j(t + \Delta t) = \Psi_j^\dagger(t + \Delta t) \cdot \left(1 + \frac{i\mathbf{H} \Delta t}{2\hbar}\right)^{-1} \cdot \left(1 - \frac{i\mathbf{H} \Delta t}{2\hbar}\right) \cdot \Psi_j(t) \cdot \Psi_j(t) = \Psi_j^\dagger(t) \cdot \Psi_j(t).$$

(61)
More recently a still better method has been introduced by Torralva. In this approach, the first-order term in a Dyson-like series for the time evolution operator $U(t + \Delta t, t)$ is written in unitary form:

$$U(t + \Delta t, t) = \left( 1 + \frac{iH}{2\hbar} \right)^{-1} \left( 1 - \frac{iH}{2\hbar} \right),$$  \hspace{1cm} (63)

where

$$H = \frac{1}{\Delta t} \int_{t}^{t+\Delta t} \mathrm{d}t' H(t'),$$  \hspace{1cm} (64)

so that again

$$U^\dagger(t + \Delta t, t) \cdot U(t + \Delta t, t) = 1.$$ \hspace{1cm} (65)

After evaluating each element of $H$ with Simpson’s rule (for example), one then obtains the electron states from

$$\Psi_j(t + \Delta t) = U(t + \Delta t, t) \cdot \Psi_j(t).$$ \hspace{1cm} (66)

With this algorithm, unitarity (i.e. orthonormality of the one-electron states $\Psi_j$) is preserved to the machine accuracy of better than $10^{-12}$. One might expect that this algorithm would give a significant improvement only when the oscillations of each wavefunction $\Psi_j(t)$ are slow compared to those of the Hamiltonian $H(t)$ but in practice the use of $H$ (rather than $H$) allows the time step to be reduced by a factor of two or more.

### 3. Results

Cis-butadiene was first simulated for 1000 fs with no laser pulse, in order to obtain the equilibrium ground state geometry. The results are in agreement with experiment [40]. The three torsional angles $\theta$, $\phi_1$ and $\phi_2$, defined by C$_1$–C$_2$–C$_3$–C$_4$, H$_5$–C$_1$–C$_2$–C$_3$ and C$_2$–C$_3$–C$_4$–H$_9$ in figure 1, are respectively 0°, 180° and 180° for the equilibrium geometry in the electronic ground state. A laser pulse with a full-width-at-half-maximum (FWHM) duration of 75 fs, centred at 4.15 eV, and with a fluence of 0.60 kJ m$^{-2}$ was used in the work of the present paper. The wavelength of the laser pulse matches the energy gap between the HOMO and LUMO of cis-butadiene calculated using the density functional approach. The fluence is selected in such a way that, with the specified pulse length, the atoms feel forces that are sufficiently strong to induce a change of geometry, but not strong enough to cause dissociation. The selection of the pulse duration is based on the recent experiments of Fuss et al. [10]. A time step of 50 as was found to give sufficient accuracy and good energy conservation.

We will first present results for cis $\rightarrow$ trans photoisomerization of butadiene, and then discuss the detailed photoisomerization mechanism as found in the simulation.

The variations in torsional angles with time are plotted in figure 2(a), with an enlarged view of the interval from 300 to 500 fs in figure 2(b). It can be seen that the butadiene molecule starts to rotate about its two terminal C–C bonds after 300 fs, and to twist simultaneously around all three C–C bonds after 330 fs. Starting from its initial geometry, butadiene has rotated through approximately
180° about each C–C bond by 500 fs (figure 2(b)). Each torsional mode then fluctuates about its new angle until the end of the simulation (figure 2(a)). These results clearly demonstrate the formation of the trans conformation of butadiene after about 500 fs. The increase in the distance between the two carbon atoms at the ends of the molecule, plotted in figure 3, provides further direct evidence for the formation of trans-butadiene: the C₁–C₄ mean intramolecular distance changes from 3.0 Å, for the cis structure, to 3.8 Å, for trans, after about 500 fs.

The energy variations for the HOMO, LUMO and LUMO +1 orbitals, and the time-dependent populations of these orbitals, are plotted in figures 4(a) and (b). An enlarged view of these results from 0 to 150 fs, corresponding to the laser
Figure 3. Variations of $C_1$–$C_4$ intramolecular distance in butadiene with time.

Figure 4. (a) Energy variations with time of HOMO (highest occupied molecular orbital), LUMO (lowest unoccupied molecular orbital) and LUMO+1 in butadiene. Note the three non-adiabatic couplings leading to electronic transitions which are indicated by arrows. (b) Electron occupation of LUMO and LUMO+1 orbitals of the butadiene molecule. Again three non-adiabatic transitions are marked by arrows.
excitation period, is shown in figures 5(a) and (b). Laser excitation promotes 0.75 electrons from HOMO to LUMO, and 0.55 electrons to LUMO+1 (figure 5(b)). Less than 0.1 electrons are excited to molecular orbitals above LUMO+1 in energy, so the behaviour of these electrons will not be discussed. The excitation of electrons to LUMO+1 mainly occurs at about 92 fs, when the energy gap between LUMO and HOMO equals 0.41 eV, matching the energy of the laser pulse used for the excitation, as can be seen in figure 5. Couplings occur among the three molecular orbitals, HOMO, LUMO and LUMO+1, shortly after 300 fs (see figure 4(a)). Examination of the changes in the occupation of the LUMO and LUMO+1 indicates that three avoided crossings shortly after the end of the laser excitation, indicated by 1, 2, 3 in figure 4(a), lead to non-adiabatic electronic transitions, again marked 1, 2, 3 in figure 4(b). These transitions change the forces on the nuclei. The energy gaps of the three non-adiabatic couplings are 0.22 eV for 1, 0.17 eV for 2 and 0.14 eV for 3. Non-adiabatic coupling 1, occurring at 338 fs, induces an electronic transition from HOMO to LUMO; 2 at 361 fs leads to a decay from LUMO to HOMO; and 3 at 458 fs yields a depopulation from

Figure 5. (a) Expanded scale of figure 4(a) from 0 to 150 fs. This is the full interval during which the laser pulse is applied. (b) Expanded scale of figure 4(b) from 0 to 150 fs.
LUMO to LUMO. From 458 fs until the end of the simulation, there are no further significant electronic transitions involving these molecular orbitals.

In order to understand the mechanism of photoisomerization in cis-butadiene, one must consider the response of the other features of the molecular geometry, including bond lengths and angles, to the excitations and de-excitations of the electrons. The variation of the central C–C bond length with time is presented in figure 6, and that of the two terminal C–C bond lengths in figures 7(a) and (b). Figure 6 reveals that the central C–C bond length shrinks after approximately 50 fs, then expands after about 150 fs, and finally starts to fall back to its initial value after 500 fs. The decrease in this C–C bond length is a consequence of the electronic excitation from HOMO to LUMO. The following increase corresponds to an excited-state to excited-state transition (from LUMO to LUMO+1), as shown in figure 5. The final decrease in the central C–C bond length is an effect of electronic depopulation, with a return to the character of a normal single bond.

On the other hand, figures 7(a) and (b) show that the electronic transitions from HOMO to LUMO and from LUMO to LUMO+1 both lengthen the C–C bonds at the ends of the molecule. The depopulation of LUMO and LUMO+1 then returns them to their normal status as relatively short double bonds.

The behaviour of the bond lengths is explained by the character of the three principal molecular orbitals [41]. In the case of the central C–C bond, the HOMO has a node with relatively small charges on the central C atoms, the LUMO has no node, and the LUMO+1 has a node with relatively large charges. The LUMO therefore gives stronger bonding than the HOMO, and the LUMO+1 weaker bonding (since it is more strongly antibonding). In the case of the terminal C–C bonds, the HOMO has no node, but both the LUMO and LUMO+1 have nodes, yielding weaker bonding.

The amplitudes of the stretching motions for both central and terminal C–C bonds are found to be much greater than before the laser excitation, demonstrating strong vibrational excitation for these modes. In addition, the frequencies of all three C–C stretching modes are found to be slightly smaller after electronic excitation, as is consistent with the bond length changes demonstrated in figures 6.
and 7. It is evident in figure 6 and in figures 7(a) and (b) that the stretching motions of all C–C bonds remain active after non-adiabatic decays.

The variations in two C–C–C bending angles are presented in figures 8(a) and (b). Similarly, the variations in two H–C–H bending angles are shown in figures 9(a) and (b), and the variations in the C₁–C₂–H₇ and C₄–C₃–H₈ bending angles (also called hydrogen migration angles in [19]) are shown in figures 10(a) and (b). It can be seen in figure 8 that the two C–C–C bending angles exhibit similar variations with time: the vibrational amplitudes of both increase sharply after approximately 400 fs, indicating that C–C–C bending vibrations are excited as electronic energy is released through the internal conversion process at 365 fs. On the other hand, as can be seen in figure 9, two H–C–H bending angles show an increase in vibrational amplitude before 150 fs, indicating that these H–C–H bending vibrations are activated by the initial laser excitation. A further increase in the amplitude of these bending modes, at approximately 200 fs, must result from intramolecular vibrational energy redistribution, since no corresponding internal conversion process is observed around this time. Both the C₁–C₂–H₇ and the C₄–C₃–H₈ bending modes (figure 10) are initially excited by the laser pulse, before

Figure 7. Variations of C₁–C₂ and C₃–C₄ bond lengths with time.
150 fs, and are further intensified at around 400 fs, again because electronic energy is released through internal conversion.

The variations in the lengths of the C\(_1\)–H\(_3\) and C\(_1\)–H\(_6\), C\(_4\)–H\(_9\), C\(_4\)–H\(_{10}\), and C\(_2\)–H\(_7\) and C\(_3\)–H\(_8\) bonds as functions of time are plotted in figures 11, 12 and 13. Figures 11(a) and (b) and figures 12(a) and (b) show that the stretching modes for the four terminal C–H bonds are activated primarily after 200 fs but before 400 fs. The energy deposited into these modes therefore comes from the excess energy of other active vibrational modes, via intramolecular vibrational energy redistribution. The further increase in the amplitude of the C\(_1\)–H\(_5\) vibration at approximately 400 fs is due to the non-adiabatic transition just before this time. All further intensification and attenuation of the stretching motions for the four terminal C–H bonds after 600 fs must result from vibrational energy redistribution. On the other hand, the C\(_2\)–H\(_7\) and C\(_3\)–H\(_8\) stretching modes (figure 13) are excited as a result of the initial laser pulse, with increases in amplitude at about 400 fs reflecting the release of electronic energy.

Figure 8. (a) Variation of C\(_1\)C\(_2\)C\(_3\) angle with time. (b) Variation of C\(_2\)C\(_3\)C\(_4\) angle with time.
The non-adiabatic transition labelled 2 (in figure 4(b)) occurs during an avoided crossing. At this time, the three C–C torsional angles $\theta$, $\phi_1$ and $\phi_2$ are $45^\circ$, $100^\circ$ and $25^\circ$ relative to their initial values. Although there are other active vibrational modes which might contribute to non-adiabatic coupling (such as stretching of both central and terminal C–C bonds, and bond-bending for $C_1$–$C_2$–H$_7$, $C_4$–$C_3$–H$_8$ and H–C–H, as well as other active vibrations not shown above), the large deviations from the ground state equilibrium values in the torsional angles indicate that avoided crossings result mainly from simultaneous rotations around three C–C bonds. Kinetic energy, resulting from the release of electronic energy via internal conversion at the avoided crossings, is distributed among C–C–C bending modes (figure 8), $C_1$–$C_2$–H$_7$ and $C_4$–$C_3$–H$_8$ bending modes (figures 10(a) and (b)), $C_1$–H$_5$ and $C_3$–H$_8$ stretching modes (figures 11(a) and 13(b)), and other vibrational modes that are not shown here.

Many calculations have been performed to study non-adiabatic couplings, involving the electronic ground state and low-lying excited states, along the various internal coordinates associated with photoisomerization of butadiene.

Figure 9.  (a) Variation of $H_5C_1H_6$ angle with time.  (b) Variation of $H_9C_4H_{10}$ angle with time.
Representative examples include: investigation of the out-of-plane deformation of the first electronically excited state by Zerbetto and Zgierski [16]; Ohmine's study of the hydrogen migration angles, CH$_2$ pyramidalization angles and C–H lengths [19]; research on CC torsions, C–C–C bending angles and C–C bond lengths by Ito and Ohmine [23]; calculations of the conformational space of three CC torsions by Robb and co-workers [17]; and investigation of the more relevant active modes by Krawczyk et al. [22]. The simulations reported in the present paper include all the atomic degrees of freedom, and therefore the observed conformational changes are a consequence of all 24 internal coordinates.

A check on energy conservation is provided by monitoring the variations in electronic and kinetic energies during the course of the simulation, as shown in figures 14(a) and (b). Figure 14(a) reveals that the electronic energy increases sharply from $-253.5$ to $-242.5$ eV during the first 150 fs, and then drops just before 400 fs and again shortly after this time. The increase in the electronic energy is a consequence of electronic excitation, as well as a shift in the energies of the

![Figure 10](image-url)  
Figure 10. (a) Variation of C$_1$C$_2$H$_7$ angle with time. (b) Variation of C$_4$C$_3$H$_8$ angle with time.
(partially) occupied electronic levels. The decrease in electronic energy before 400 fs is a result of a non-adiabatic transition at the avoided crossing at 361 fs, and the decrease after 400 fs is due to depopulation of the LUMO$^+$ orbital. Figure 14(b) demonstrates that the kinetic energy of atomic motion increases from 0.0 to 0.7 eV during the first 150 fs (as the laser pulse produces repulsive interatomic forces via electronic excitation), and exhibits further increases before and after 400 fs (as electronic energy is released via non-adiabatic transitions).

Based on the results presented above, we can now outline the detailed mechanism for cis $\rightarrow$ trans photoisomerization in butadiene following a femtosecond-scale laser pulse. There is first a series of electronic excitations: primarily HOMO $\rightarrow$ LUMO and LUMO $\rightarrow$ LUMO$^+$. These excitations, and the resultant change in bonding, cause both the central and terminal C–C bond lengths to be enlarged. The change in bonding also causes the C–C bond stretching vibrations, and other vibrational modes, to be excited. The excess kinetic energy of these vibrational modes is then shared with the torsional modes, centred at the

Figure 11. (a) Variation of C$_1$–H$_5$ bond length with time. (b) Variation of C$_1$–H$_6$ bond length with time.
three C–C bonds, via intramolecular vibrational energy redistribution. Consequently, the molecule twists about its three C–C bonds. As it twists, the electronic levels experience avoided crossings with relatively small energy gaps, where the excited electrons can undergo downward transitions by creating vibrational excitations. After reaching the ground state, the molecule continues to rotate around its central C–C bond and one of the terminal C–C bonds until the trans conformation is attained.

There have been numerous theoretical investigations of the photoisomerization process in butadiene. Many one-dimensional studies and more accurate ab initio calculations suggest that non-adiabatic decay is induced by the CC torsions. Ito and Ohmine further proposed that this decay occurs at three partially twisted C–C bond conformations [23]. Olivucci et al. investigated an entire conformational space of three torsions, and proposed that non-adiabatic decay is dominated by a conical intersection induced by the triple CC torsions [17]. The simulation presented in the present paper confirms these proposals. In addition, however, we

![Figure 12](image-url)
show here that cis-butadiene in the excited electronic state twists around two terminal C–C bonds first, and then simultaneously rotates around all three C–C bonds. After depopulation of excited electronic states at avoided crossings, the molecule continues to rotate about its central C–C bond and one of the terminal C–C bonds, until the \textit{trans} conformation is achieved.

4. Summary
In this work, we have investigated the \textit{cis} \rightarrow \textit{trans} photoisomerization of butadiene, by performing realistic dynamical simulations. Our method, semi-classical electron-radiation-ion dynamics (SERID), is fully described in the text. The molecule was subjected to a laser pulse with a FWHM pulse duration of 75 fs, centred at 4.15 eV, and with a fluence of 0.60 kJ m\(^{-2}\). The results demonstrate that electrons are excited to both the LUMO and LUMO+1 levels. While in an
electronically excited state, the molecule first rotates about two terminal C–C bonds, and then simultaneously around all three C–C bonds. One can clearly observe the non-adiabatic interaction of electronic levels at avoided crossings, where electrons make downward transitions with a release of energy to the vibrational motion of the atoms. It is these transitions which are ultimately responsible for stabilizing the new structure, although the detailed dynamics is quite intricate.

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Figure 14. (a) Variation of electronic energy with time. (b) Variation of kinetic energy with time.
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