

Electronic optical response of molecules in intense fields: Comparison of TD-HF, TD-CIS, and TD-CIS(D) approaches

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Time-dependent Hartree-Fock (TD-HF) and time-dependent configuration interaction (TD-CI) methods with Gaussian basis sets have been compared in modeling the response of hydrogen molecule, butadiene, and hexatriene exposed to very short, intense laser pulses (760 nm, 3 cycles). After the electric field of the pulse returns to zero, the molecular dipole continues to oscillate due to the coherent superposition of excited states resulting from the nonadiabatic excitation caused by the pulse. The Fourier transform of this residual dipole gives a measure of the nonadiabatic excitation. For low fields, only the lowest excited states are populated, and TD-CI simulations using singly excited states with and without perturbative corrections for double excitations [TD-CIS(D) and TD-CIS, respectively] are generally in good agreement with the TD-HF simulations. At higher field strengths, higher states are populated and the methods begin to differ significantly if the coefficients of the excited states become larger than ~ 0.1 . The response of individual excited states does not grow linearly with intensity because of excited state to excited state transitions. Beyond a threshold in the field strength, there is a rapid increase in the population of many higher excited states, possibly signaling an approach to ionization. However, without continuum functions, the present TD-HF and TD-CI calculations cannot model ionization directly. The TD-HF and TD-CIS simulations are in good accord because the excitation energies obtained by linear response TD-HF [also known as random phase approximation (RPA)] agree very well with those obtained from singly excited configuration interaction (CIS) calculations. Because CIS excitation energies with the perturbative doubles corrections [CIS(D)] are on average lower than the CIS excitation energies, the TD-CIS(D) response is generally stronger than TD-CIS. © 2007 American Institute of Physics. [DOI: 10.1063/1.2743982]

I. INTRODUCTION

A variety of strong field effects are observed when molecules are subject to intense femtosecond and picosecond laser pulses.¹ These effects include field tunneling and barrier-suppression ionization,²⁻⁵ above-threshold ionization,^{6,7} generation of higher-order harmonic emissions,⁸⁻¹² field-induced resonant enhancement of electronic absorption,¹³⁻¹⁵ and nonadiabatic multielectron excitation.¹⁶⁻¹⁹ When the electric fields of the laser are comparable with those sampled by valence electrons, the response of the molecule cannot be treated by perturbative methods. Under these circumstances, the numerical simulation of the behavior of the electronic density interacting with intense electrical fields can be helpful in understanding some of the strong field effects.

Atomic systems have been studied extensively, but the understanding of molecular strong field processes is far from complete. The most detailed and accurate molecular results are available for H_2^+ and H_2 . Bandrauk and co-workers²⁰⁻⁴¹ have used numerical integration of the time-dependent

Schrödinger equation (TDSE) for one and three dimensional fix nuclear simulations and full dimensional electron-nuclear dynamics of H_2 in intense laser fields to study the single and double ionization, electron recollision ionization, and higher harmonic generation. For larger systems, some approximations are needed. Chu and co-workers⁴²⁻⁴⁸ have studied many electron atoms and diatomics using time-dependent generalized pseudospectral methods, self-interaction corrected density functional theory, and Floquet matrix techniques. Mukamel and co-workers^{49,50} have simulated π electron dynamics in octatetraene with a semiempirical Hamiltonian and have modeled ionization saturation intensities in a multielectron system in a finite one dimensional box. Cederbaum and co-workers^{51,52} have used a multielectron wave packet dynamics approach to investigate hole migration following ionization. Klamroth and co-workers⁵³⁻⁵⁵ have used optimal control theory and time-dependent configuration interaction with single excitations (TD-CIS) to shape short, intense pulses for state-selective excitation of *N*-methyl-quinoline and employed TD-CIS(D) to simulate dipole switching in lithium cyanide. In previous papers we

have used time-dependent Hartree-Fock (TD-HF) theory to simulate the response of a series of polyenes, polyacenes, and their cations to short, intense laser pulses.⁵⁶⁻⁵⁹

The molecules of interest in strong field chemistry can be quite sizable, and practical computational methods may require some compromises between efficiency and accuracy. For simulations not involving ionization, TD-HF and TD-CIS are the two most promising methods for modeling the electronic response of a molecule involving more than a few atoms. The suitability of time-dependent density functional theory (TD-DFT) will be considered in a separate study, since there is some question whether present functionals can handle charge transfer effects properly for the large distortions of the electron density that can develop in strong field situations. TD-HF and TD-CIS should give the same results in the limit of very small fields but will begin to differ as the fields are increased toward the strong field regime. The TD-CIS(D) method includes perturbative doubles corrections to the CIS excitation energies^{60,61} but uses the same transition dipoles as CIS. The purpose of the present paper is to compare the behavior of TD-HF, TD-CIS, and TD-CIS(D) methods with Gaussian basis sets for a few conjugated molecules in intense laser pulses and to obtain some understanding of the advantages and limitations of these three approaches in the absence of ionization. Of the many simulations carried out, examples are selected to illustrate where the three approaches begin to differ.

II. METHODS

The time-dependent Schrödinger equation in a.u. is

$$i \frac{d\psi(t)}{dt} = \hat{H}(t)\psi(t). \quad (1)$$

If the wave function is expanded in terms of the eigenfunctions of the time independent, field-free Hamiltonian,

$$\hat{H}_0\varphi_i = \omega_i\varphi_i, \quad (2)$$

$$\psi(t) = \sum C_i(t)\varphi_i, \quad (3)$$

the time-dependent Schrödinger equation reduces to a set of coupled differential equations for the time-dependent coefficients,

$$i \frac{dC_i(t)}{dt} = \sum_j H_{ij}(t)C_j(t), \quad (4)$$

where $H_{ij}(t) = \langle \varphi_i | \hat{H} | \varphi_j \rangle$. In the dipole approximation, the matrix elements of the field-dependent Hamiltonian in Eq. (4) can be expressed in terms of the field-free energies ω_i , transition dipole moments $D_{ij} = \langle \varphi_i | \hat{r} | \varphi_j \rangle$, and the electric field $\mathbf{e}(t)$,

$$\begin{aligned} H_{ij}(t) &= \langle \varphi_i | \hat{H} | \varphi_j \rangle = \langle \varphi_i | \hat{H}_0 | \varphi_j \rangle + \langle \varphi_i | \hat{r} | \varphi_j \rangle \cdot \mathbf{e}(t) \\ &= \omega_i \delta_{ij} + D_{ij} \cdot \mathbf{e}(t). \end{aligned} \quad (5)$$

For the full solution of the TDSE, the sum in Eq. (4) extends over all bound states and the continuum. For practical applications, finite basis sets are usually used, and the

sum needs to be restricted to a suitable subset of states. For example, TD-CISD includes the ground state and all singly and doubly bound excited states, while TD-CIS includes the ground state and only the singly excited states. Adding perturbative doubles corrections for correlation to the CIS excitation energies yields the TD-CIS(D) approach. Continuum states are needed to simulate ionization, but this is beyond the scope of the present study.

Within the TD-CIS and TD-CISD methods, it may be desirable to limit the total number of states used. Increasing the number of states included until no further change is seen in the simulation is one means of determining whether the number of states is adequate. Calculating the static polarizability in the sum over states formalism provides a different measure of convergence,

$$\alpha = 2 \sum_i \mathbf{D}_{0i} \mathbf{D}_{i0} / \omega_i. \quad (6)$$

The time-dependent Hartree-Fock method starts with the time-dependent Schrödinger equation and restricts the wave function to a single Slater determinant but allows the one electron orbitals to be a function of time,

$$\psi(t) = \hat{A}[\phi_1(t)\phi_2(t)\cdots\phi_i(t)], \quad (7)$$

where \hat{A} is the antisymmetrization operator. The equations for the molecular orbitals $\phi_i(t)$ can be written in terms of the Fock operator,

$$i \frac{d\phi_i(t)}{dt} = \hat{F}(t)\phi_j(t). \quad (8)$$

The molecular orbitals can be expanded in terms of basis functions χ_μ ,

$$\phi_i(t) = \sum_\mu c_{\mu,i}(t)\chi_\mu. \quad (9)$$

The density matrix can be constructed from the product of the molecular orbital coefficients

$$P'_{\mu\nu} = \sum_i c_{\mu,i} c_{\nu,i}^\dagger. \quad (10)$$

The corresponding Fock matrix is given by

$$\mathbf{F}'_{\mu\nu}(t) = \langle \chi_\mu | F(t) | \chi_\nu \rangle. \quad (11)$$

In general, the basis functions are not orthonormal; hence the overlap matrix $S_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle$ is not the identity. The density matrix and the Fock matrix can be transformed from the atomic orbital (AO) basis (\mathbf{P}' and \mathbf{F}') into an orthonormal basis (\mathbf{P} and \mathbf{F}) by a transformation matrix \mathbf{V} ,

$$\mathbf{P} = \mathbf{V}\mathbf{P}'\mathbf{V}^T \text{ and } \mathbf{F} = \mathbf{V}^{-T}\mathbf{F}'\mathbf{V}^{-1}. \quad (12)$$

The present study uses Löwdin orthonormalization, $\mathbf{V} = \mathbf{S}^{1/2}$. In an orthonormal basis, the TD-HF equation for the density matrix is

$$i \frac{d\mathbf{P}(t_i)}{dt} = [\mathbf{F}(t_i), \mathbf{P}(t_i)]. \quad (13)$$

The field-dependent Fock matrix can be written in terms of the field-free Fock matrix $\mathbf{F}_0(t)$ and the dipole moment integrals in the AO basis, $\mathbf{d}'_{\mu\nu} = \langle \chi_\mu | \hat{\mathbf{r}} | \chi_\nu \rangle$,

$$\mathbf{F}'(t) = \mathbf{F}'_0(t) + \mathbf{d}' \cdot \mathbf{e}(t). \quad (14)$$

Note that the field-free Fock matrix also depends on time due to the time dependence of the density matrix \mathbf{P} .

In the present study, we use a linearly polarized and spatially homogeneous external field,

$$\mathbf{e}(r, t) \approx \mathbf{E}(t) \sin(\omega t + \varphi). \quad (15)$$

This is a good approximation for the laser field because typical wavelengths are much larger than molecular dimensions. The present simulations use a short trapezoidal pulse lasting ~ 7 fs for $\omega = 0.06$ a.u. (760 nm) in which $|\mathbf{E}(t)|$ increases linearly to $|\mathbf{E}_{\max}|$ at the end of the first cycle, remains at $|\mathbf{E}_{\max}|$ for one cycle, and then decreases linearly to zero by the end of the next cycle.

$$\begin{aligned} \mathbf{E}(t) &= (\omega t/2\pi)\mathbf{E}_{\max} & \text{for } 0 \leq t \leq 2\pi/\omega, \\ \mathbf{E}(t) &= \mathbf{E}_{\max} & \text{for } 2\pi/\omega \leq t \leq 4\pi/\omega, \\ \mathbf{E}(t) &= (3 - \omega t/2\pi)\mathbf{E}_{\max} & \text{for } 4\pi/\omega \leq t \leq 6\pi/\omega, \\ \mathbf{E}(t) &= 0 & \text{for } t < 0 \text{ and } t > 6\pi/\omega. \end{aligned} \quad (16)$$

The instantaneous dipole is a convenient probe to monitor the response of the molecule to the laser pulse. For the TD-CI approach, the instantaneous dipole moment is

$$\boldsymbol{\mu}(t) = \sum_A Z_A \mathbf{R}_A - \sum_{ij} C_i^\dagger(t) \mathbf{D}_{ij} C_j(t), \quad (17)$$

where Z_A and \mathbf{R}_A are the nuclear charges and positions, and \mathbf{D}_{ij} are the transition dipole matrix elements. For the TD-HF approach, the instantaneous dipole is given by

$$\boldsymbol{\mu}(t) = \sum_A Z_A \mathbf{R}_A - \text{tr}(\mathbf{d}' \mathbf{P}'(t)), \quad (18)$$

where \mathbf{d}' are the dipole moment integrals in the AO basis.

After the electric field has returned to zero, the instantaneous dipole may continue to oscillate if the wave function is a coherent superposition of the ground and excited states. The power spectrum obtained by Fourier transforming this oscillating residual dipole can reveal which excited states contribute to the instantaneous dipole. This could also be interpreted as the emission spectrum from the superposition of states resulting from the laser pulse. For the TD-CI methods, the time dependence of the residual dipole after the pulse is given by

$$\boldsymbol{\mu}(t) = \sum_A Z_A \mathbf{R}_A - \sum_{ij} C_i^\dagger(t_f) \mathbf{D}_{ij} C_j(t_f) e^{i(\omega_i - \omega_j)(t - t_f)}, \quad (19)$$

where t_f is a time after the field has returned to zero. The Fourier transform of Eq. (19) gives discrete lines, whereas the numerical Fourier transform of the TD-HF or TD-CI instantaneous dipole over a finite simulation interval is neces-

sarily broadened by the limited number of data points in the interval (i.e., the linewidths are *not* an indication of the lifetimes).

The electronic structure calculations were carried out with the development version of the GAUSSIAN 03 software package.⁶² As in our earlier paper,⁵⁶ hydrogen molecule was calculated with a bond length of 0.733 13 Å using the 6-311++G(*d,p*) basis and the aug-cc-pVTZ basis^{63,64} plus three extra sets of *sp* diffuse functions with exponents of 0.01, 0.005, and 0.0025. The electric field of the pulse was directed along the bond axis. Similar to our previous studies,^{57,58} butadiene, hexatriene, and their cations were calculated with the 6-31G(*d,p*) basis set at the optimized geometry of the all *trans* neutral molecules, with the field directed along the long axis of the molecule, specifically along the vector connecting the end carbons. The unitary transform method described earlier was used for the integration of the TD-HF equations.⁵⁶ Field-free excitation energies and transition dipole matrix elements were calculated with the CIS,⁶⁰ CIS(D),⁶¹ and SAC-CI (Ref. 65) methods (for CISD). MATHEMATICA 5.0 (Ref. 66) was used to integrate the TD-CI equations and analyze the results. The TD-HF and TD-CI integrations were carried out with a step size of 0.05 a.u. (0.0012 fs) for 14 000 steps (16.8 fs).

III. RESULTS AND DISCUSSION

A. Hydrogen molecule

The response of hydrogen molecule to intense oscillating electric fields was simulated with the TD-CIS, TD-CIS(D), TD-CISD, and TD-HF methods. As in our previous TD-HF studies,⁵⁶ two different basis sets were used for H₂. Since continuum functions are not included in these basis sets, the simulations are not intended to model ionization processes. The 6-311++G(*d,p*) basis set has a total of 14 basis functions for H₂. The six lowest excited states of Σ_g or Σ_u symmetry were chosen for the CIS and CISD calculations. A much larger basis was constructed by adding three sets of diffuse *sp* functions to the aug-cc-pVTZ basis, for a total of 70 basis functions. After the linear dependencies in the basis set were removed, this generated 66 singly excited states (all symmetries) for the CIS calculation. For the CISD calculation, the lowest 34 Σ_g and 34 Σ_u states were chosen. The molecule was subject to a short pulse (as described in Sec. II) with the electric field oriented along the axis. The frequency was chosen to be $\omega = 0.06$ a.u. (760 nm), corresponding to the commonly employed Ti:sapphire laser. The short trapezoidal pulse shape is the same as used in our previous studies.

For field strengths up to $E_{\max} = 0.07$ a.u. (1.7×10^{14} W cm⁻²), the TD-CIS, TD-CIS(D), TD-CISD, and TD-HF simulations with the 6-311++G(*d,p*) basis yield essentially the same results. Experimentally, H₂ ionizes rapidly at higher field strengths. However, for testing purposes, the field for the 6-311++G(*d,p*) simulation was increased to 0.12 a.u. so that some differences could be discerned, as illustrated in Fig. 1. The top row shows the electric field of the pulse, the instantaneous dipole computed by TD-HF, and the Fourier transform of the residual dipole oscillations after the

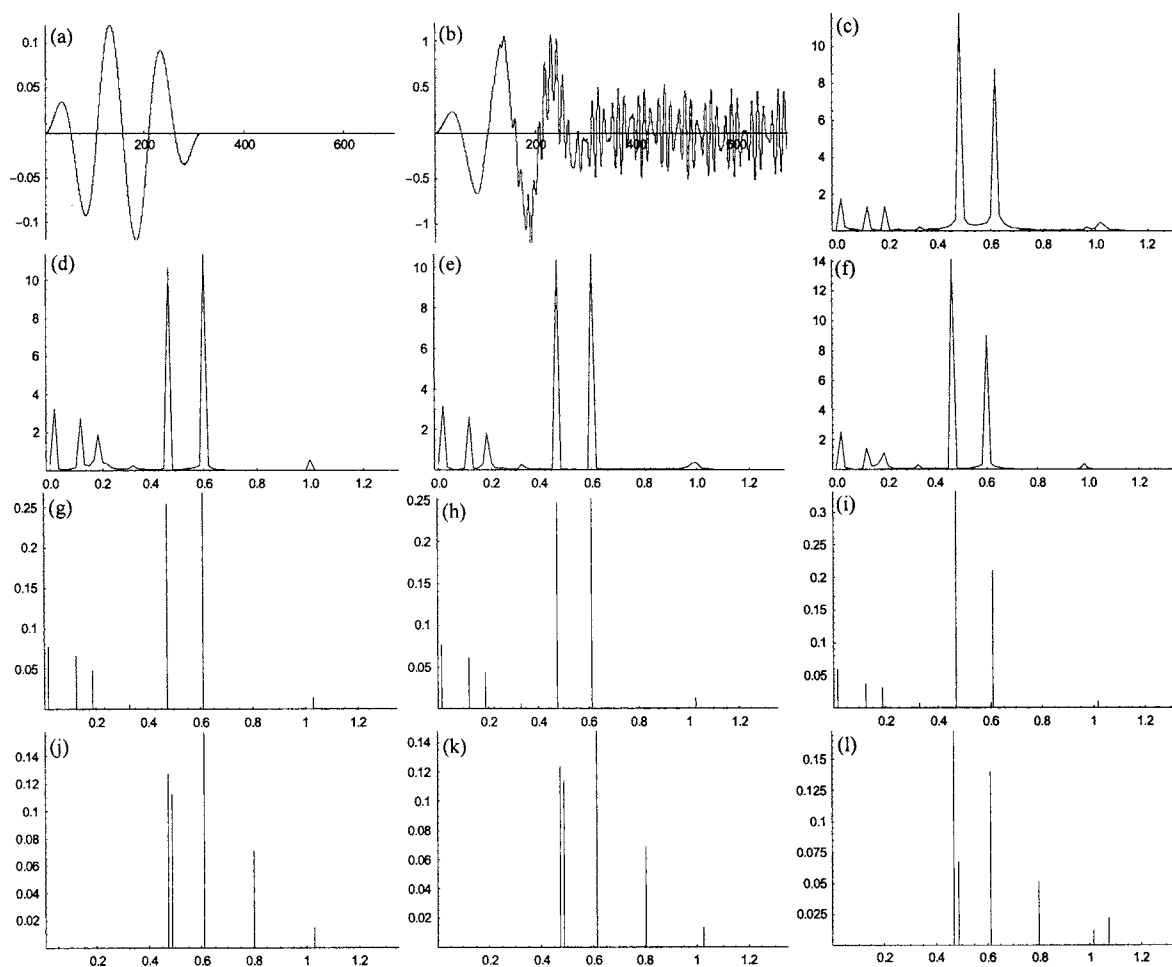


FIG. 1. Simulation of H_2 in an oscillating electric field (energies and time in a.u., $E_{\max}=0.12$ a.u. and $\omega=0.06$ a.u.) with the 6-311++G(d,p) basis. Top row: (a) electric field, (b) the instantaneous dipole calculated by TD-HF, and (c) the Fourier transform of the residual dipole after the field has returned to zero calculated by TD-HF. Second row: the Fourier transform of the residual dipole calculated by (d) TD-CIS, (e) TD-CIS(D), and (f) TD-CISD. Third row: contributions to the oscillation of the residual dipole computed from the wavefunction at the end of the simulation by (g) TD-CIS, (h) TD-CIS(D), and (i) TD-CISD. Bottom row: magnitude of the excited state coefficients in the wave function at the end of the simulation by (j) TD-CIS, (k) TD-CIS(D), and (l) TD-CISD.

field has returned to zero. The dipole does not follow the field adiabatically during the pulse and continues to oscillate after the pulse has returned to zero. The latter can be interpreted as a nonadiabatic excitation. The dipole responses computed by TD-CIS, TD-CIS(D), and TD-CISD are nearly identical to the TD-HF results on this scale; however, small differences can be seen in the Fourier transform of the residual oscillations after the pulse has returned to zero (second row of Fig. 1). The TD-CIS and TD-CIS(D) results are almost identical, since the doubles correction shifts the excitation energies by only a very small amount for H_2 . The Fourier transforms of the TD-CISD and TD-HF results are very similar but are slightly different than the TD-CIS and TD-CIS(D) results, in that the heights of the two dominant peaks are no longer the same. For the TD-CI methods, the information contained in the Fourier transform of the residual dipole oscillations can be obtained directly from the wave function at any time after the pulse has returned to zero. The third row in Fig. 1 shows these contributions to the oscillation of the dipole plotted as a function of energy and can be compared directly to the Fourier transforms in the second row. The agreement is excellent, and the data ob-

tained directly from the wave function are not subject to the broadening that necessarily accompanies the Fourier transform of a limited amount of data (however, for the TD-HF simulations, only the Fourier transform can be obtained readily). The last row of Fig. 1 shows the magnitudes of the coefficients of the zero field states in the wave function at the end of the simulation. Not all states contribute directly to the oscillations of the dipole, and some oscillations of the dipole occur at frequencies corresponding to the differences between excited state energies. The good agreement between the TD-CISD and TD-HF results indicates that six excited states are sufficient for H_2 with this small basis set and ignoring ionization.

Simulations with the larger basis set at field strengths of $E_{\max}=0.07$ and 0.12 a.u. are shown in Figs. 2 and 3. This basis set provides considerably more flexibility for the electron density, and residual oscillations in the dipole contain many more Fourier components. Nevertheless, it is not possible to model ionization with this basis as it does not contain continuum functions. In tests with a field strength of 0.12 a.u., the TD-CISD simulations with 48 and 58 excited states gave the same results for the instantaneous dipole and

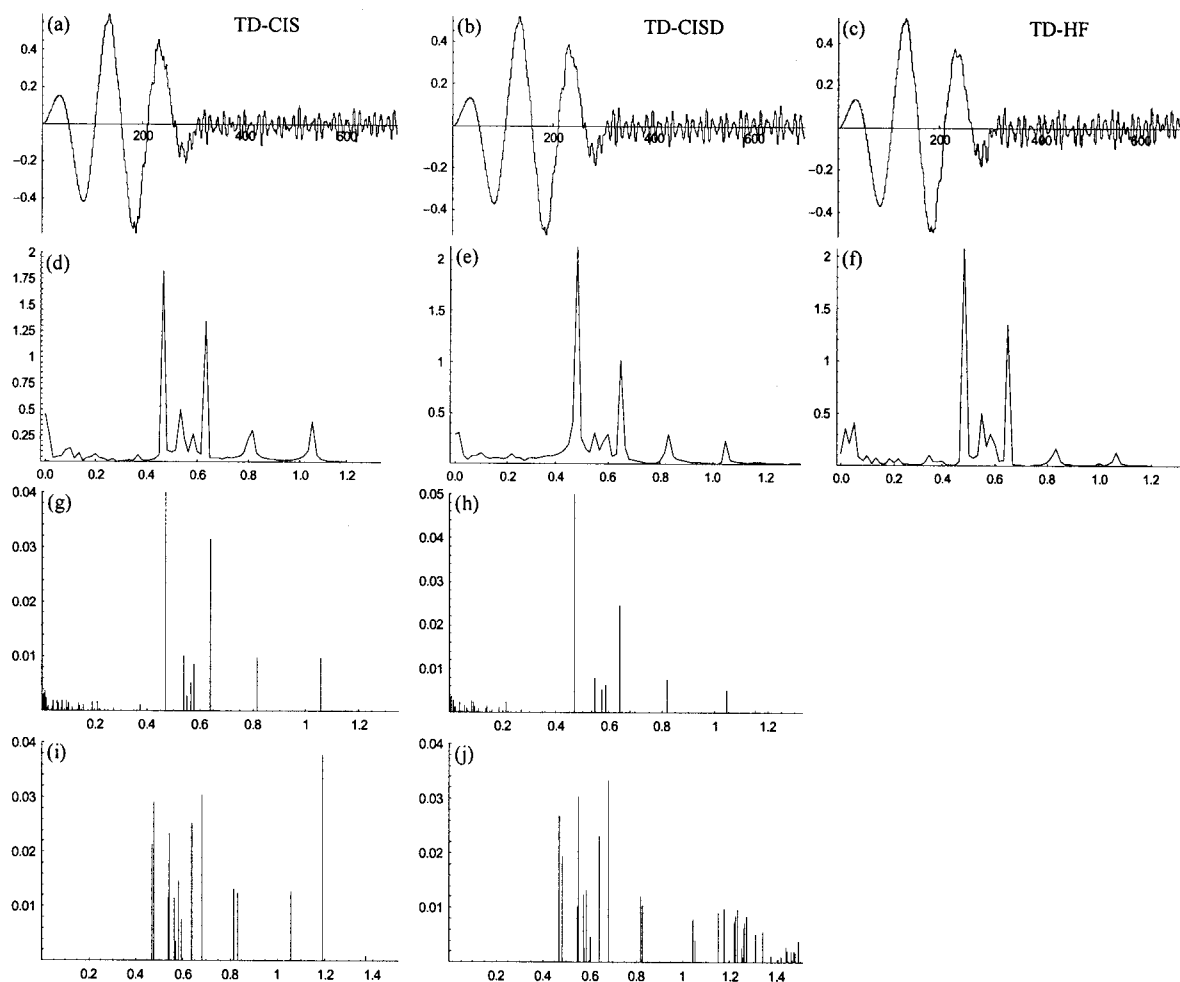


FIG. 2. Simulation of H_2 in an oscillating electric field (energies and time in a.u., $E_{\max}=0.07$ a.u. and $\omega=0.06$ a.u.) with the aug-pVTZ basis plus three additional sets of sp diffuse functions. Top row: instantaneous dipole calculated by (a) TD-CIS, (b) TD-CISD, and (c) TD-HF. Second row: Fourier transform of the residual dipole after the field has returned to zero calculated by (d) TD-CIS, (e) TD-CISD, and (f) TD-HF. Third row: contributions to the oscillation of the residual dipole computed from the wave function at the end of the simulation by (g) TD-CIS and (h) TD-CISD. Bottom row: magnitude of the excited state coefficients in the wave function at the end of the simulation by (i) TD-CIS and (j) TD-CISD.

the Fourier transform of the residual dipole as obtained with 68 excited states. This indicates that the TD-CISD calculations of the instantaneous dipole and the Fourier transform of the residual dipole are well converged with respect to the number of excited states for the present pulse conditions. Since H_2 is a two electron system, TD-CISD calculations constitute a full solution of the time-dependent Schrödinger equation within the basis set and can be used as a standard for comparison with the TD-HF and TD-CIS results. As shown in Fig. 2 for a field strength of 0.07 a.u. the TD-CIS, TD-CISD, and TD-HF results are in good agreement. Compared to the simulations at the same field strength with the smaller basis set, there are numerous low frequency contributions arising from differences between excited states not seen with the smaller basis set. Although the TD-CIS and TD-CISD dipole responses appear nearly the same, the wave function components differ significantly. In particular, Fig. 2(j) illustrates that the TD-CISD calculation has numerous high energy components coming from the doubly excited states not included in the TD-CIS simulation. However, their effects on the dipole response under these conditions are small. When the field is raised to 0.12 a.u., the differences

between TD-CIS, TD-CISD, and TD-HF are quite noticeable (see Fig. 3). Although the three simulations are dominated by the first dipole allowed excited state, there are significant differences in the low frequency region: compared to the TD-CISD results, TD-CIS has higher intensity peaks while TD-HF has lower intensity peaks. There are also noticeable differences in the intensities of the peaks in the higher frequency region. Several of the coefficients in the wave function are greater than 0.2 (last row of Fig. 3), whereas in the simulation with $E_{\max}=0.07$ a.u., all of the coefficients were less than 0.05 and the three methods produced very similar results (Fig. 2).

The effects of the field strength on the Fourier transform of the residual dipole and the degree of nonadiabatic excitation are summarized in Fig. 4. At lower fields, the oscillations of the residual dipole come primarily from a few of the lowest excited states. As the field strength increases, the contributions do not grow linearly with the intensity (square of the field strength). At the higher fields, more states contribute, but the lowest dipole allowed excited state still dominates. There are also numerous contributions at lower frequencies arising from transition dipoles between excited

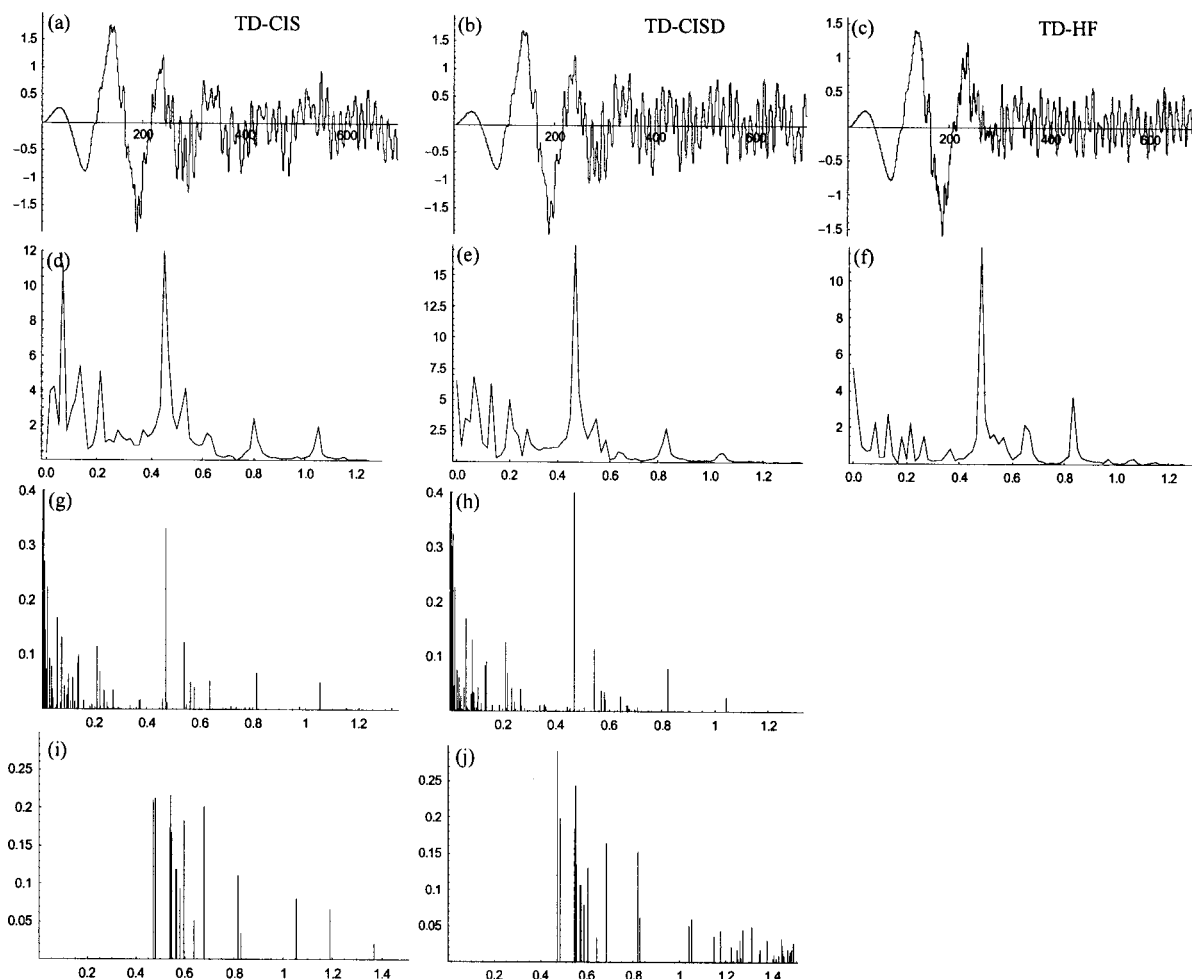


FIG. 3. Simulation of H_2 in an oscillating electric field (energies and time in a.u., $E_{\max}=0.12$ a.u. and $\omega=0.06$ a.u.) with the aug-pVTZ basis plus three additional sets of sp diffuse functions. Top row: instantaneous dipole calculated by (a) TD-CIS, (b) TD-CISD, and (c) TD-HF. Second row: Fourier transform of the residual dipole after the field has returned to zero calculated by (d) TD-CIS, (e) TD-CISD, and (f) TD-HF. Third row: contributions to the oscillation of the residual dipole computed from the wave function at the end of the simulation by (g) TD-CIS and (h) TD-CISD. Bottom row: magnitude of the excited state coefficients in the wave function at the end of the simulation by (i) TD-CIS and (j) TD-CISD.

states. The weights (squares of the coefficients) of the excited states in the wave function after the electric field has returned to zero provide a more direct measure of the nonadiabatic excitations produced by the pulse. A number of the low energy states have large weights, not just the ones contributing to the residual dipole. As the field becomes larger, more states are excited, but closer inspection shows that the weights do not increase linearly with the intensity. The weights of the higher excited states remain small by comparison to the low energy states.

B. Butadiene

For molecules such as butadiene and larger, the solution of the time-dependent Schrödinger equation using a full set of excited states (i.e., full CI) is not practical. Even expansion in terms of all single and double excitations (i.e., CISD) may be impractical for larger molecules, since the number of states grows with the fourth power of the size of the molecule (however, because of the sparsity of the Hamiltonian, the cost of a propagation step grows only as the fifth power). The simulations involving H_2 indicate that if the field strength is not too high, TD-CIS and TD-HF can produce

similar results. Exploratory calculations with H_2 also suggest that a subset of the excitations may be sufficient and that single excitations contribute much more to the behavior of the wave function than double excitations. Before comparing TD-CIS with TD-HF for butadiene, it will be necessary to determine how many singly excited states are needed for the simulation.

The top row of Fig. 5 compares the CIS and CIS(D) excitation energies with the linear response TD-HF excitation energies [also known as the random phase approximation (RPA)]. As expected, the CIS and RPA excitation energies are in excellent agreement, suggesting that the TD-HF and TD-CIS simulations should be in good agreement. The CIS(D) excitations are on average 12% lower than RPA, as a result of correlation contributions from perturbative doubles corrections to the excitation energies. These correlation corrections also introduce considerable spread into the comparison with the (uncorrelated) TD-HF excitations (some caution is needed if these corrections become too large). Similar comparisons between RPA, CIS, and CIS(D) are found for the monocation and for the dication (not shown). The bottom row of Fig. 5 compares the CIS and TD-HF spectra for the

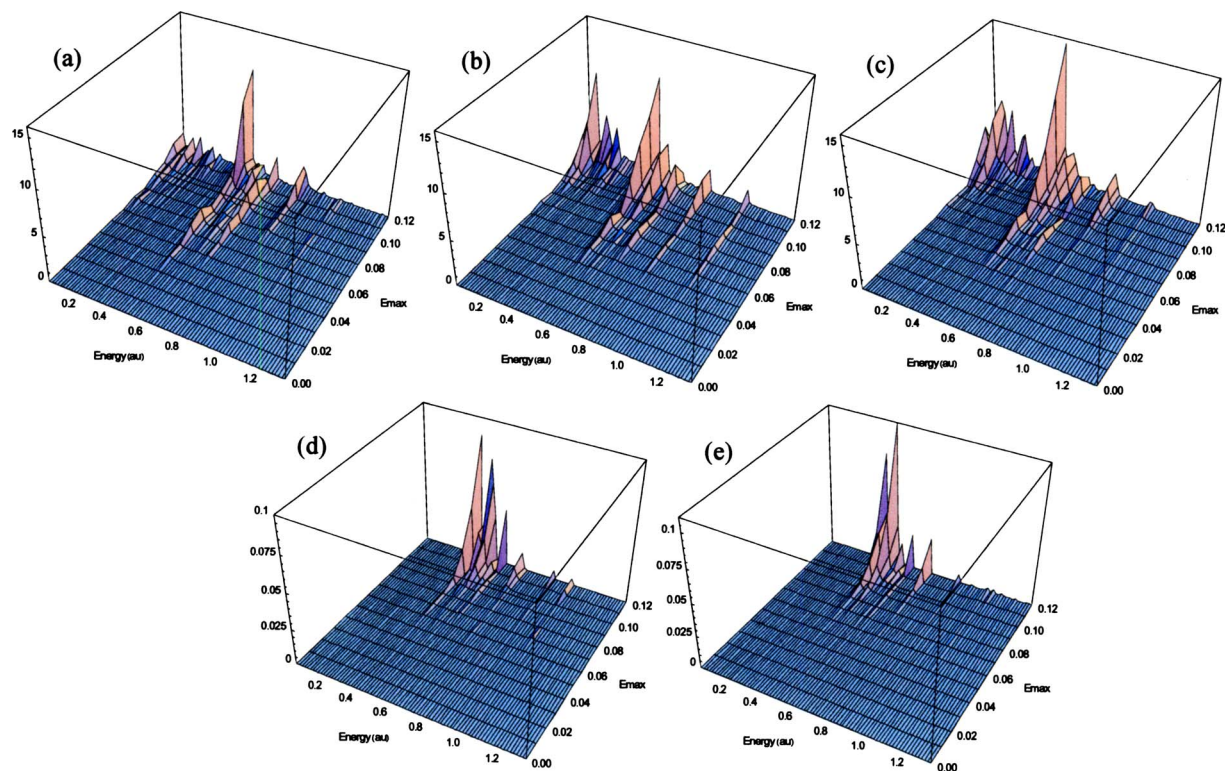


FIG. 4. Response of the hydrogen molecule to increasing field strength: Fourier transform of the residual dipole obtained by (a) TD-HF, (b) TD-CIS, and (c) TD-CISD, and the squares of the wave function coefficients obtained by (d) TD-CIS and (e) TD-CISD ($\omega=0.06$ a.u., aug-pVTZ basis plus three additional sets of *sp* diffuse functions).

electric field directed along the vector connecting the end carbons. Overall, the spectra agree very well, but the intensities for TD-HF are a bit lower, particularly for the first excitation.

Table I compares the static dipole polarizabilities calculated as a second derivative of the Hartree-Fock and coupled clusters with singles and doubles (CCSD) energies and by the sum over states approach, Eq. (6), using the CIS, CIS(D),

and TD-HF excitation energies and transition dipoles. As the number of states is increased to 160, the polarizabilities of neutral butadiene appear to be converged to about 1%–2%. The CIS(D) results overestimated the polarizability more than the CIS results, whereas TD-HF underestimates the HF static polarizability. The behavior for the dication is similar (not shown). The polarizability for the monocation is larger than for the neutral, primarily because of smaller excitation

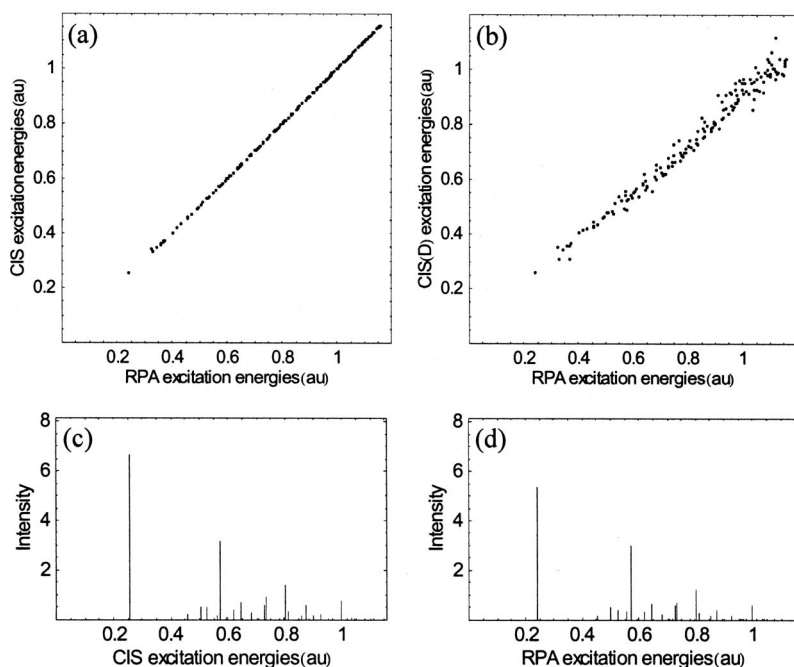


FIG. 5. Comparison of excitation spectra for butadiene calculated with the 6-31G(*d,p*) basis set: (a) CIS excitation energies vs RPA or linear response TD-HF ($E_{\text{CIS}}=0.9987E_{\text{RPA}}+0.0033$ a.u.) and (b) CIS(D) energies vs RPA ($E_{\text{CIS}}=0.8848E_{\text{RPA}}+0.0229$ a.u.). (c) The CIS spectrum polarized along the long axis of the molecule and (d) the corresponding RPA spectrum.

TABLE I. Comparison of static polarizabilities for butadiene calculated by Hartree-Fock and CCSD, and by second order perturbation theory using the CIS, CIS(D), and TD-HF excited states [6-31G(*d,p*) basis set].

Theory	No. of states	α_{xx}	α_{xy}	α_{yy}	α_{zz}
Butadiene neutral					
HF		37.797	7.578	77.060	15.819
CCSD		38.069	6.416	66.300	15.454
CIS	80	36.022	9.625	80.506	3.150
	120	38.410	8.517	85.914	12.471
	160	39.063	8.255	86.835	12.576
CIS(D)	80	39.149	9.371	82.081	3.511
	120	41.790	8.129	88.046	13.213
	160	42.516	7.835	89.066	13.325
RPA ^a	80	32.132	8.856	70.522	2.699
	120	33.836	8.075	74.525	10.485
	160	34.393	7.876	74.993	10.564
Butadiene monocation					
UHF		56.338	37.629	110.120	14.881
UCCSD		46.965	24.809	87.985	14.657
UCIS	80	34.722	23.356	69.678	1.457
	120	43.137	22.232	77.526	3.898
	160	44.815	23.292	80.976	4.515
UCIS(D)	80	36.348	23.717	72.279	1.674
	120	45.467	22.470	80.818	4.538
	160	47.327	23.635	84.654	5.236
RPA ^a	80	42.873	38.882	94.670	1.575
	120	49.986	37.850	101.660	3.356
	160	51.321	38.650	104.746	3.882

^aLinear response TD-HF.

energies as discussed in our earlier papers.^{58,67} Second order perturbation theory seems to converge a bit more slowly for the monocation, and the trend for CIS and CIS(D) is to values significantly lower than the HF polarizability.

Figure 6(a) shows the effect of increasing the number of states from 70 to 160 in the TD-CIS simulation for neutral butadiene subject to a pulse with a field strength of $E_{\max} = 0.05$ a.u. States with energies up to 0.5 a.u. and with wave function coefficients with magnitudes greater than 0.002 appear to be well converged. Similar behavior is found for the monocation and the dication at field strengths of 0.03 a.u.; convergence at higher fields is somewhat slower. The response to a short pulse seems to converge noticeably quicker than the static polarizability as the number of singly excited states is increased. The remaining simulations for butadiene and its cations were carried out with 160 singly excited states. About 100 of these states have transition dipoles in the plane of the molecule and are coupled to the field.

Figure 7 shows the Fourier transform of the residual oscillations of the dipole for butadiene neutral, monocation, and dication. The experimental ionization saturation intensity for butadiene is probably somewhat higher than for hexatriene [8.9×10^{12} W cm⁻² for a 44 fs full width at half maximum (FWHM) pulse⁶⁸]. For the present, much shorter pulse (~ 4.5 fs FWHM), the same intensity should result only a small amount of ionization for neutral butadiene. The top row of Fig. 7 shows that for neutral butadiene with a field strength of $E_{\max} = 0.05$ a.u. the results are very similar for TD-CIS and TD-HF, while the TD-CIS(D) simulation has a

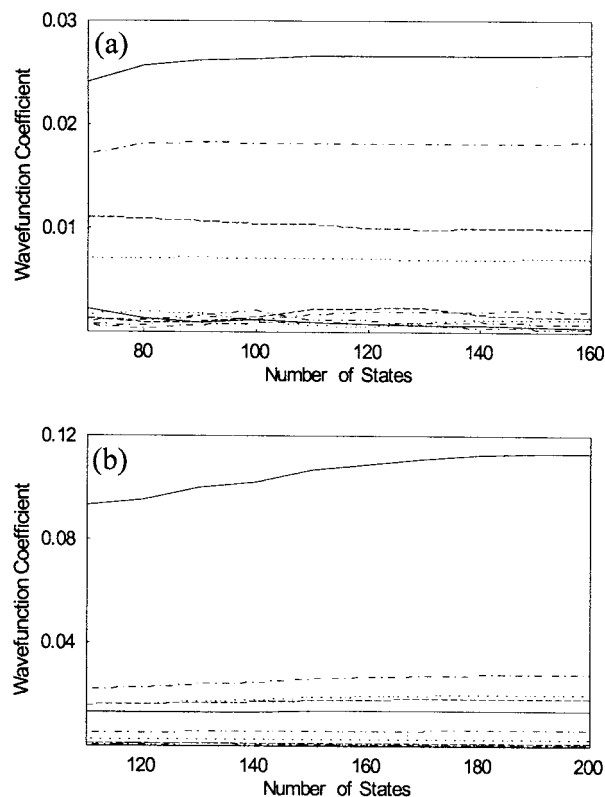


FIG. 6. Wave function coefficients as a function of the number of states included in the TD-CIS simulation. The magnitudes of the ten largest states are shown after the pulse has returned to zero: (a) neutral butadiene with a field strength of 0.05 a.u. and (b) neutral hexatriene with a field strength of 0.03 a.u.

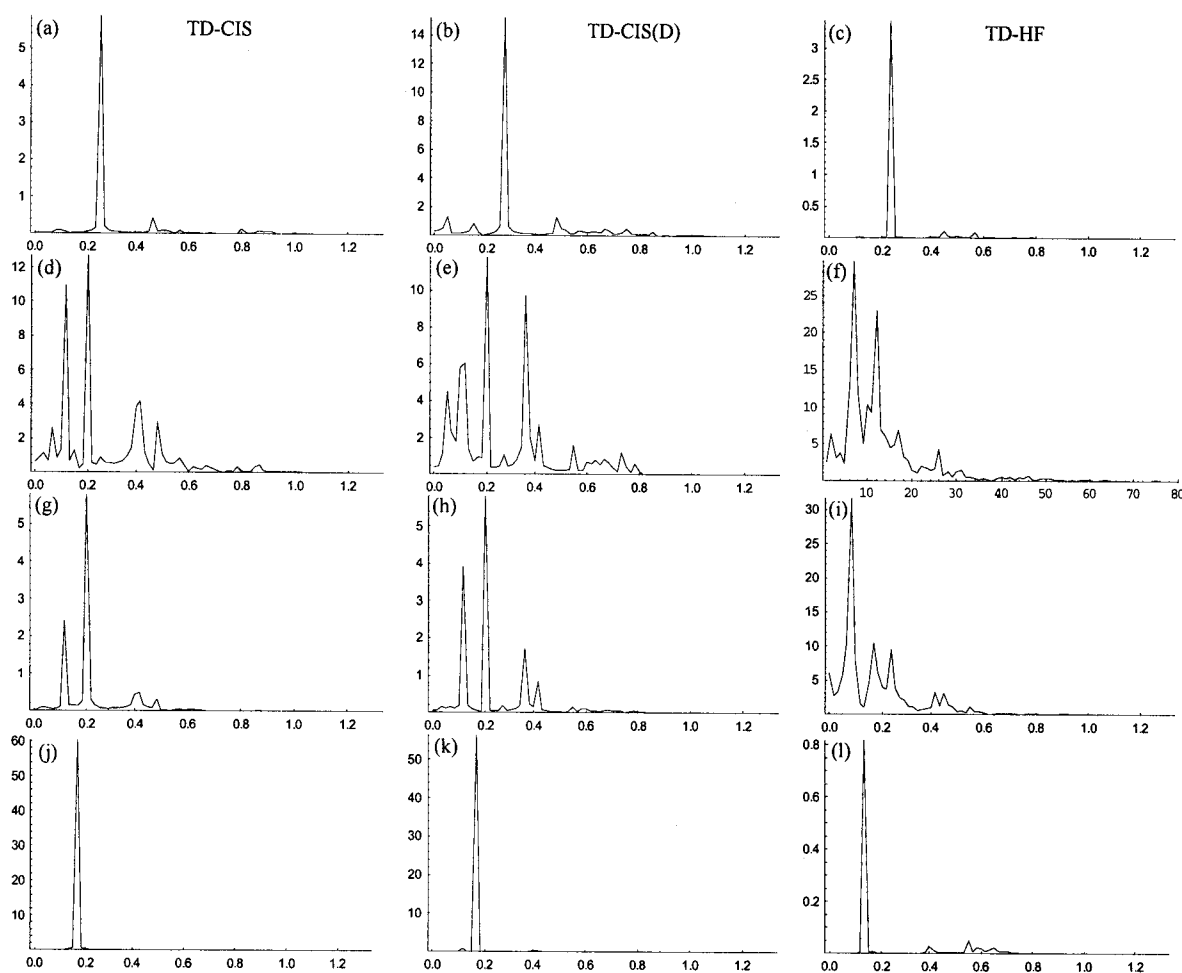


FIG. 7. Fourier transform of the residual dipole after the field has returned to zero for butadiene calculated with the 6-31G(*d,p*) basis set: neutral (top row), monocation (middle two rows), and dication (bottom row) for TD-CIS (left column), TD-CIS(D) (middle column), and TD-HF (right column). Energies in a.u.: first two rows were calculated with $E_{\text{max}}=0.05$ a.u. and $\omega=0.06$ a.u., and the last two rows were calculated with $E_{\text{max}}=0.03$ a.u. and $\omega=0.06$ a.u.

number of additional peaks. Explorations with a reduced number of states indicate that this is because the perturbative doubles correction lowers the third and fourth in-plane excitations by 0.03–0.06 a.u. For the monocation (Fig. 7 second row), TD-CIS and TD-HF have the same two dominant peaks but differ in the height of many of the smaller peaks. The TD-CIS(D) simulation again has another peak that is significantly stronger than seen in the TD-CIS results. The open shell monocation is much more polarizable, and a field strength of $E_{\text{max}}=0.05$ a.u. leads to a wave function with excited state coefficients larger than 0.1. When the field is reduced to $E_{\text{max}}=0.03$ a.u. (third row of Fig. 7), the largest coefficient for TD-CIS is 0.07 and the agreement between TD-CIS and TD-CIS(D) is much better, but the TD-HF Fourier transform still has a much stronger peak. The lowest excited state calculated by linearized TD-HF (RPA) has a transition dipole that is 26% larger than for CIS and an excitation energy that is 20% lower, which may explain the difference in peak heights. The Fourier transforms of the residual dipole for the dication (bottom row of Fig. 7) are much simpler than those for the monocation and are dominated by a single peak corresponding to the lowest excited state. However, the TD-HF peak is much smaller than the TD-CIS and TD-CIS(D) peaks. The transition dipole is 15%

smaller for TD-HF, accounting for a part of this difference. The coefficients for the lowest excited state in the TD-CIS and TD-CIS(D) wave functions are quite large (~ 0.3) because of near-resonance effects. When the frequency of the field is reduced by 15%, the peak height and wave function coefficients in the TD-CIS and TD-CIS(D) simulations are reduced by an order of magnitude. As in the monocation case, both the differences in the transition dipole and in the excitation energy contribute to the difference in degree of nonadiabatic excitation seen in the TD-CI and TD-HF simulations.

Figure 8 illustrates the effect of the field strength on the Fourier transform of the residual dipole and the degree of nonadiabatic excitation. As in the hydrogen molecule case, the response is dominated by the lowest energy state. However, unlike hydrogen, where the three methods yield very similar responses, in neutral butadiene the TD-CIS(D) response is significantly greater than TD-CIS and TD-HF. As a function of field strength, the TD-CIS and TD-CIS(D) results also have more structure than TD-HF. Both the Fourier transforms of the residual dipoles and the wave function weights for the TD-CI calculations show that for field strengths greater than 0.08 a.u. (2.2×10^{14} W cm $^{-2}$), there is a rapid

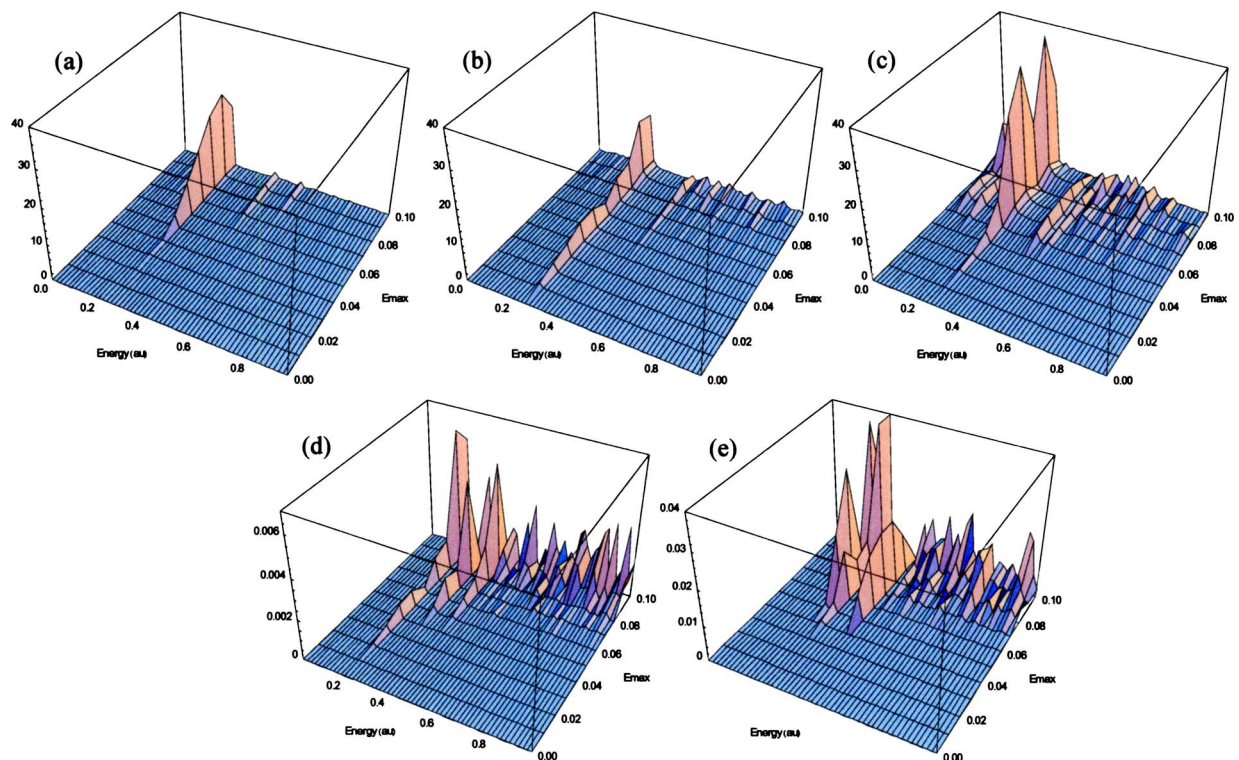


FIG. 8. Response of butadiene to increasing field strength: Fourier transform of the residual dipole obtained by (a) TD-HF, (b) TD-CIS, and (c) TD-CIS(D) and the squares of the wave function coefficients obtained by (d) TD-CIS and (e) TD-CIS(D) [$\omega=0.06$ a.u., 6-31G(d,p) basis].

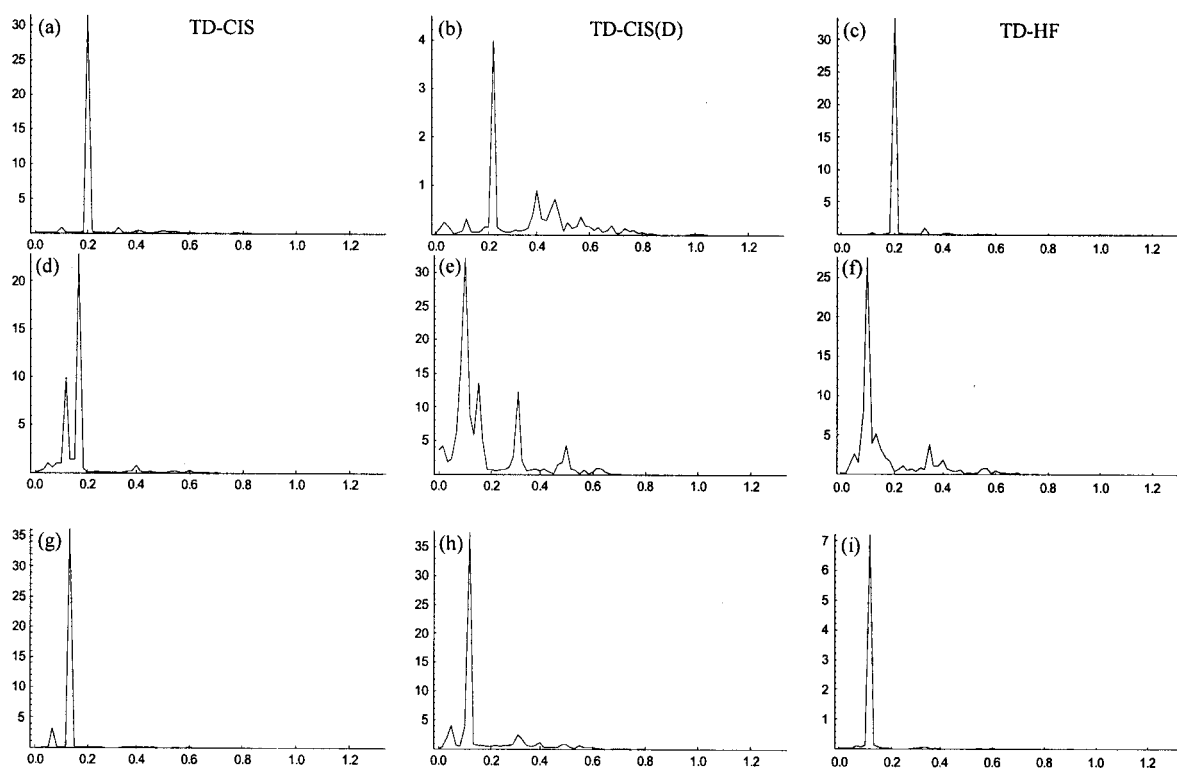


FIG. 9. Fourier transform of the residual dipole after the field has returned to zero for hexatriene [$\omega=0.06$ a.u., 6-31G(d,p) basis]: neutral (top row, $E_{\max}=0.03$ a.u.), monocation (middle row, $E_{\max}=0.02$ a.u.), and dication (bottom row, $E_{\max}=0.02$ a.u.) for TD-CIS (left column), TD-CIS(D) (middle column), and TD-HF (right column).

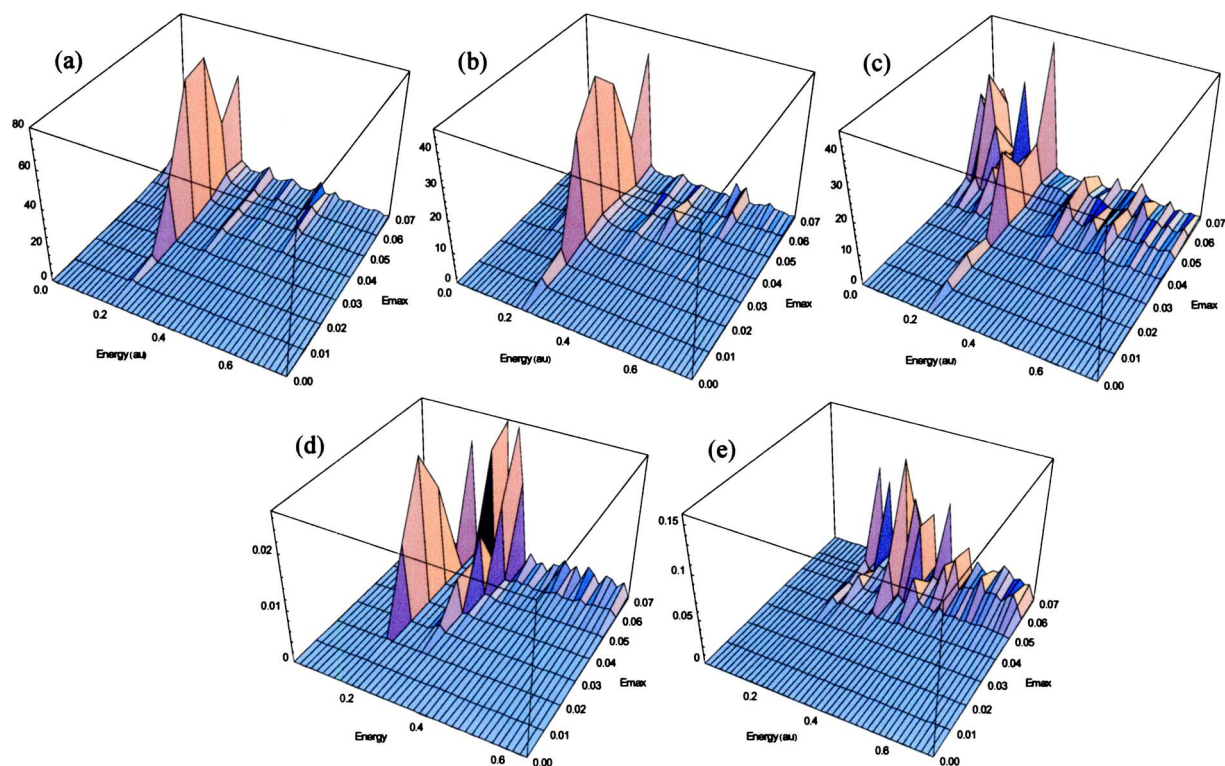


FIG. 10. Response of hexatriene to increasing field strength: Fourier transform of the residual dipole obtained by (a) TD-HF, (b) TD-CIS, and (c) TD-CIS(D) and the squares of the wave function coefficients obtained by (d) TD-CIS and (e) TD-CIS(D) [$\omega=0.06$ a.u. 6-31G(*d,p*) basis].

increase in the contribution from numerous higher energy states. There is a corresponding decrease in the weight of the ground state that is proportional to the fifth or sixth power of the field strength. Within the limited basis set of the present calculations, the sudden increase in the population of many higher excited states may be a diagnostic for the onset of ionization.

C. Hexatriene

Similar to butadiene, there is excellent agreement between the CIS and RPA spectra for hexatriene neutral, monocation, and dication. As a result of electron correlation from the perturbative doubles corrections, the CIS(D) excitations energies are on average 22% lower than CIS or RPA for the neutral molecule. The corrections are somewhat larger for the monocation and the dication. With 200 singly excited states, the in-plane polarizabilities computed by second order perturbation theory are converged to about 3%–5% for the neutral molecule and the dication, and about 4%–8% for the monocation. Figure 6(b) illustrates the effect of increasing the number of states in the TD-CIS simulation for neutral hexatriene subject to a pulse with $E_{\max}=0.03$ a.u. States with energies up to 0.45 a.u. and wave function coefficients with magnitudes greater than 0.002 appear to be well converged with 200 states. The monocation and the dication behave similarly at field strengths of 0.02 a.u.; convergence at higher fields is somewhat slower. The simulations displayed in Figs. 9 and 10 were carried out with 200 states. This corresponds to 90–117 states with transition dipoles in the plane of the molecule.

The Fourier transforms of the residual oscillations of the dipole are shown in Fig. 9. For a 44 fs FWHM pulse, the experimental ionization saturation intensity for hexatriene is 8.9×10^{12} W cm $^{-2}$.⁶⁸ The shorter pulse and lower intensity used for neutral hexatriene should lead to only a small amount of ionization. For $E_{\max}=0.03$ a.u., the results from the TD-CIS, TD-CIS(D), and TD-HF calculations on neutral hexatriene are dominated by the lowest excited state, but the peak height for TC-CIS(D) is smaller by factor of 8. For the mono- and dications, smaller fields are needed for reasonable agreement between the different methods. Even with $E_{\max}=0.02$ a.u. the TD-CIS(D) simulation for the monocation differs markedly from the TD-CIS and TD-HF results. The largest excited state coefficients at the end of the simulation are 0.06–0.15 for the lowest few excited states in the TD-CIS calculation, but the TD-CIS(D) calculation has more states with large coefficients at higher energies. For the dication, the TD-CIS and TD-CIS(D) simulations are in good agreement, but the peak height for TD-HF is smaller by a factor of 5. The largest wave function coefficients are for the lowest few excited states and are in the range of 0.1–0.14. For stronger fields, the Fourier transforms of the residual dipole differ more significantly, higher excited states become more prominent, and these have excited state coefficients that are significantly larger than 0.1.

The effects of varying the field strength on the response of neutral hexatriene are shown in Fig. 10 for both the Fourier transform of the residual dipole and the weights of the excited states in the wave function at the end of the simulation. At low intensities, the response is dominated by the lowest excited state. As the field is increased, the contribu-

tion of the lowest state increases but not linearly with the intensity. At higher fields, the contribution of the lowest excited state decreases as higher excited states become populated. The excited state coefficients are much larger for the TD-CIS(D) simulation. Similar to butadiene, there is a rapid increase in the population of many of the excited states for both TD-CIS and TD-CIS(D) at fields greater than 0.05–0.07 a.u. possibly signaling the approach of ionization.

IV. SUMMARY

This study has compared TD-CIS, TD-CIS(D), and TD-HF calculations of the response of hydrogen molecule, butadiene, and hexatriene subject to short, intense laser pulses. The results were analyzed by examining the nonadiabatic excitation caused by the pulse, as manifested by the residual oscillations of the dipole after the electric field of the pulse had returned to zero. Since the population of individual excited states can vary significantly and nonuniformly with the field strength, it may be better to consider general trends when comparing the three methods. Of the numerous simulations carried out, examples in Figs. 1–10 were chosen to illustrate conditions where the methods begin to differ.

If the fields are low enough, only the lowest few excited states are populated, and if the coefficients are less than ~ 0.1 , then the TD-CIS, TD-CIS(D), and TD-HF methods are generally in good agreement. Such conditions are most likely encountered for field strengths that do not cause ionization. At higher field strengths, higher states are populated both directly (e.g., if they have a nonzero transition dipole with the ground state) and through transitions from the lowest excited state (e.g., if the transition dipole with the ground state is zero). The response does not grow linearly and depends on the intricate details of the excitation energies and transition dipoles—seemingly small changes can cause sizable differences in the coefficients of the wave function. While there are no sharp resonances with such short, intense pulses, changing the frequency of the field by 10%–20% can change the degree of nonadiabatic excitation by an order of magnitude.

As the field is increased further, the population of the lowest excited state can decrease as excitations from this state to higher states become important. While the weight of individual excited states can vary markedly, the depopulation of the ground state is a more uniform function of the field. For neutral butadiene, it is proportional to the fifth or sixth power of the field. Beyond some threshold in the field strength, there is a rapid increase in the population of many higher excited states, possibly leading to ionization. However, the TD-HF and TD-CI calculations cannot properly model the ionization that will occur at these higher field strengths unless continuum functions are included in the basis set.

The TD-HF method agrees better with TD-CIS than with TD-CIS(D) because the linearized TD-HF (RPA) and CIS excitation energies are in very good agreement. The response is generally stronger for TD-CIS(D) than for TD-CIS, because the CIS(D) energies are on average lower than the CIS energies. However, the perturbative doubles corrections can

be rather large, and some caution may be required. The importance of including explicit double excitation will be considered in a future study and may help resolve this question.

In terms of computational efficiency, TD-HF (and TD-DFT) scales approximately as the third power of the system size for the small molecules considered here (and linearly for much larger systems). However, there is a large prefactor that depends linearly on the number of integration steps. On the other hand, CIS and CIS(D) calculations formally depend on the fifth power of the system size. However, these calculations need only be done once for a particular geometry and charge state. The integration of the TD-CI equations depends quadratically on the number of states and linearly on the number of time steps. Thus, the TD-CI approach can be advantageous for exploring different pulse shapes, since the expensive CIS or CIS(D) calculations need be done only once.

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