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Transient Absorption Spectroscopy of Butadiene by Time-Dependent Configuration Interaction Method

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Abstract

We perform time-dependent configuration-interaction single-excitation (TDCIS) calculations to investigate the responses of the π -electron wave functions of 1,3-butadiene to an intense near-IR laser pulse (26 fs, 800 nm, 10^{13} W/cm²) by simulating the transient absorption induced by an ultrashort vacuum ultraviolet (VUV) light pulse (2.4 fs, 180 nm, 10^{11} W/cm²).

Introduction

Ultrafast molecular dynamics in intense laser fields has been one of the most attractive research subjects in recent years. By the technique of the attosecond transient absorption spectroscopy, in which molecular systems interacting with a femtosecond near-infrared (IR) laser are probed by a sub-femtosecond extreme ultraviolet (XUV) pulse at different time delays [1], we can investigate the dynamical motion of electrons in the ultrashort time scale. In the present study, we investigate the responses of the π -electron wave functions of 1,3-butadiene, a fundamental π -conjugated system whose π electron distribution is delocalized along the carbon chain skeleton [2], to an intense near-IR laser field by the time-dependent configuration interaction (TDCI) method [3]. We demonstrate that the transient absorption of an ultrashort vacuum ultraviolet (VUV) light pulse can reveal how the electronic states respond to the intense near-IR laser pulse.

Computational Methodology

In order to solve the time-dependent Schrödinger equation by the TDCI method, a time-dependent electronic wave function is expressed as

$$\Psi(t) = \sum_{n=1}^N C_n(t) \phi_n, \quad (1)$$

where $C_n(t)$ is a time-dependent CI coefficient of the n -th state, and ϕ_n is an electronic eigenstate of the molecular Hamiltonian. In the calculation, the total number N of the electronic states is set to be $N = 8$, that is, the electronic ground state and seven electronically excited states are included. The energies of the eight electronic states and the transition dipole moments among them are calculated by the configuration interaction singles method [4] using GAMESS. The polarization directions of the VUV and near IR laser fields are set to be parallel to the molecular a axis. The delay-dependent response function, describing a response of the system to the near IR pulse modulated by the VUV pulse, is given as

$$\tilde{S}(\omega, \tau) = 2 \operatorname{Im}[\tilde{d}(\omega, \tau) \tilde{\epsilon}^*(\omega, \tau)] \quad (\omega > 0), \quad (2)$$

where $\tilde{d}(\omega, \tau)$ is the Fourier transform of the time-dependent dipole moment, and $\tilde{\varepsilon}(\omega, \tau)$ is the Fourier transform of the two-color electric fields composed of the near IR and VUV pulses.

Results and Discussion

We obtain the temporal variations of the populations in the first, third and fourth electronically excited states of 1,3-butadiene in the presence of an ultrashort near-IR intense laser field (26 fs, 800 nm, 10^{14} W/cm²) by solving the time-dependent Schrödinger equation using a computer code we have developed. The results shown in Fig. 1 show that the population in the ground state is transferred mainly to the first excited state through the π - π^* transition from the HOMO to the LUMO, and only slightly to the third and fourth excited states. In order to probe the time-dependent population transfer processes to these three electronically excited states through the interaction with the near-IR laser pulse, we introduce a VUV light pulse (2.4 fs, 180 nm, 10^{11} W/cm²) at different time delays with respect to the near-IR laser pulse (26 fs, 800 nm, 10^{13} W/cm²), and calculate the transient absorption induced by the VUV light pulse. The resultant transient absorption spectrum is shown in Fig. 2 as a function of the time delay. The negative and positive time delays mean respectively that the VUV light pulse arrives before and after the near-IR laser pulse. As shown in Fig. 2, the absorption profiles appearing at around 7 eV corresponds to one-photon absorption of the VUV light pulse from the ground state to the first electronically excited state. It is shown that the formation of the light-dressed states of 1,3-butadiene by the interaction with the intense near-IR laser pulse appears as the complex profile in the transient absorption spectrum, which varies in a characteristic manner in the delay time range where the near-IR and VUV light pulses overlap.

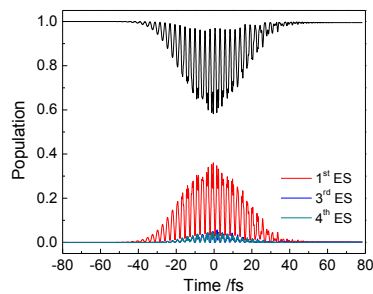


Fig. 1. The populations in the ground and three electronically excited states of *trans*1,3-butadiene in the intense near-IR laser field (26 fs, 800 nm, 10^{14} W/cm²).

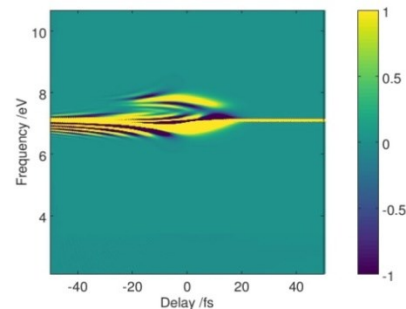


Fig. 2. The transient absorption spectrum of 1,3-butadiene as a function of the time delay of the VUV light pulse (2.4 fs, 180 nm, 10^{11} W/cm²) from the near-IR laser pulse (26 fs, 800 nm, 10^{13} W/cm²).

References

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