

## Laser Induced Dissociation Control of $H_2^+$ and $H_3^{2+}$

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**Abstract.** Laser induced dissociation control of the symmetric diatomic molecular ion  $H_2^+$  and the triatomic molecular ion  $H_3^{2+}$  is discussed. The simulation results demonstrate that a long-wavelength terahertz or mid-infrared laser pulse can be used to control the electrons of the dissociative states after the excitation of an ultrashort ultraviolet (UV) laser pulse. For  $H_2^+$ , there exists an effective time, which increases with increasing pulse duration of the UV laser pulse, for controlling the molecular dissociation. For the electrons of the  $1s\sigma_g$  state, they move along the polarization direction of the dissociation control electric field. In contrast, for the electrons of the  $2p\sigma_u$  state, they move in the opposite direction to that of the electric force. And for the triatomic molecule  $H_3^{2+}$ , the electron dissociation control can also be realized by changing the central wavelength of the exciting UV pulse.

### 1. Introduction

Coherent control of electrons and fragments in chemical reactions and photoelectron processes has attracted a great deal of interest. One of the main goals has been to find a way to selectively break and form molecular bonds in photochemical reactions [1–3]. As for searching the underlying mechanism in realizing electron localization control during the dissociation process, several solution routes have been proposed, including the mixture of the  $1s\sigma_g$  and  $2p\sigma_u$  states [4], the interference between the  $2p\sigma_u$  and  $3s\sigma_g$  states [5], and the superposition of the  $2p\pi_g$  and  $2p\pi_u$  states [6], and so on. In addition, the other quantum coupled equations [7–9] or laser-induced Stark shift effect [10–12] have also ever been used to reveal the dissociation control mechanism.

A number of theoretical and experimental studies on laser-molecule interactions have been conducted and focused on the molecular ion  $H_2^+$ , which is the simplest system having general properties of molecules. Theoretical studies have clarified that there are several dissociation mechanisms of  $H_2^+$ , such as bond softening, resonant excitation, and Coulomb explosion [13–16]. These mechanisms have been experimentally observed by utilizing pulsed lasers [17,18].

When the interaction laser pulse is very short, several new phenomena may be found, such as the enhanced high order harmonic generation, and the generation of a single attosecond pulse [19–21]. When an ultrashort ultraviolet (UV) laser pulse, with 228nm center wavelength, is used to excite the electron of the initial ground  $1s\sigma_g$  state onto the first dissociative  $2p\sigma_u$  state of the molecular ion  $H_2^+$ , through a one-photon process. The simulation results show that the dissociation ratio taken with 0.754fs laser pulse (the duration of the 228nm laser pulse, 1 optical cycle) can be about up to 6.9 times higher than for 3.02 fs laser pulse (4 optical cycles), due to the electron capture of the high vibrational bound states. The effective dissociation control time window of  $H_2^+$  is increasing with the increasing pulse duration of the exciting laser pulse. Compared with the results obtained with a 7.9fs 228nm laser pulse as we adopted in our previous work [22], both the total dissociation probability and the dissociation control ratio are improved when the exciting UV pulse is changed into a one-cycle

pulse, under the dissociation of a mid-infrared (MIR) laser pulse, due to the reducing of the effective dissociation control time window.

When a terahertz (THz) laser pulse is used to steer the electron motion after  $H_2^+$  is irradiated by an ultrashort UV laser pulse. The numerical simulation demonstrates that the ionized electron is pulled out along the polarization direction of the electric field, in contrast, the electrons in the dissociative state move in the opposite direction to that of the electric force [23]. For the dissociation of the asymmetric molecules of  $H_3^+$  and  $HeH_2^+$ , this counter-intuitive result can also be found when the two different dissociation channels  $H_3^+ + n\gamma \rightarrow H_2 + p$  and  $H_3^+ + n\gamma \rightarrow H_2^+ + H$ , and  $HeH_2^+ + n\gamma \rightarrow He + p$  and  $HeH_2^+ + n\gamma \rightarrow \alpha + H$ , for  $H_3^+$  and  $HeH_2^+$  are investigated, respectively [24].

It is well known that the linear triatomic molecular ion  $H_3^{2+}$  does not exist in the field-free case. However, the one-electron linear  $H_3^{2+}$  can be stabilized at high intensities and frequencies, due to high nonlinear electron-field interactions [25]. The linear molecular ion  $H_3^{2+}$  can also exist in a strong magnetic field, and the direction of the molecular axis is parallel to the direction of the magnetic field [26]. Furthermore, the collision between  $H^+$  and  $H_2^+$  or the dissociative ionization of  $H_3^+$  can obtain  $H_3^{2+}$ , too [27].

Compared with the simplest double-well molecular ion  $H_2^+$  and its isotopes, the linear molecular ion  $H_3^{2+}$  includes three nuclei along the molecular axis. The simulation results show that the electron localization ratio of the middle proton is dependent on the central frequency and peak electric field amplitude of the external linearly polarized UV laser pulse. The electron localization ratio of the dissociation states of the middle proton increases from 0.3% to 50.9%, by optimizing the central frequency and peak electric field amplitude of the external UV laser pulse. Besides, a direct current (dc) electric field can be used to steer the electron motion after the excitation of an UV laser pulse. The symmetry electron localization distribution is broken seriously, as a result of the dressing effect of the dc electric field. The electrons of the dissociation states of the dressed-down potential well move opposite to the dc electric field force, and captured by the middle potential well. 68.8% electrons of all the dissociation states can be steered onto the middle proton with the variation of the amplitude of the dc electric field [28].

This paper is organized as follows: section 2 describes briefly the model systems and the parameters of the external electric fields we are using. In section 3.1, the numerical results for the exploration of the pulse duration dependence landscape of electron dynamics in

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the photodissociation of  $H_2^+$  is studied. Section 3.2 describes the direction of the electron motion of  $H_2^+$  in the laser induced dissociation localization. And the dissociation control of the triatomic molecule ion  $H_3^{2+}$  is discussed in section 3.3. Finally, section 4 contains a brief summary and conclusions.

## Theoretical methods

We use a reduced-dimensional model for the molecular ions in the calculation. The molecular axis is assumed to be parallel to the polarization direction of the external laser fields. And the single-electron model is considered. For the symmetric linear  $H_3^{2+}$  molecular ion, the middle proton  $P_1$  is set at the center of the coordinate system. The inter-nuclear distance of  $P_3$  and  $P_2$  to  $P_1$  is  $R_1=R_2=R/2$ . That is, the external laser pulses are assumed to have no effect on the motion of the protons. Here  $P_2$  and  $P_3$  are the protons locating on each side of  $P_1$ . And  $R$  is the relative inter-nuclear distance between  $P_2$  and  $P_3$ . (And then) we can use the one-dimensional (1D) non-Born-Oppenheimer time-dependent Schrödinger equation (TDSE) to do the simulation [22–24]. The corresponding TDSE can be written as ( $\hbar=m_e=1.0$  in atomic unit (a.u.), which are used throughout the paper unless otherwise stated)

$$i \frac{\partial}{\partial t} \varphi(R, z; t) = [T(R, z) + V_0(R, z) + W(z, t)] \varphi(R, z; t), \quad (1)$$

where  $T(R, z)$  is the field-free Hamiltonian of the system.  $V_0(R, z)$  stands for the soft-core Coulomb interaction and  $W(z, t)$  indicates the interaction of the particle with the external laser pulses. Through this paper  $z$  represents the electronic coordinate with respect to the center of mass of the two/three nuclei, respectively. And for  $H_2^+$ ,  $R$  is the relative inter-nuclear distance.

For our model, the kinetic energy in Eq. (1) reads

$$T(R, z) = -\frac{1}{m_p} \frac{\partial^2}{\partial R^2} - \left( \frac{2m_p + m_e}{4m_p m_e} \right) \frac{\partial^2}{\partial z^2}, \quad (2)$$

here  $m_e$  and  $m_p$  are the electron mass and proton mass ( $m_p=1837$ ), respectively.

For  $H_2^+$ , the Coulomb potential is

$$V_0(R, z) = -\frac{1}{\sqrt{(z+R/2)^2 + \alpha}} - \frac{1}{\sqrt{(z-R/2)^2 + \alpha}} + \frac{1}{\sqrt{R^2 + \beta}}. \quad (3)$$

And for the molecular ion  $H_3^{2+}$ , the Coulomb potential can be expressed as

$$V_0(R, z) = -\frac{1}{\sqrt{(z+R/2)^2 + \alpha}} - \frac{1}{\sqrt{(z-R/2)^2 + \alpha}} - \frac{1}{\sqrt{z^2 + \alpha}} + \frac{3}{\sqrt{R^2 + \beta}}. \quad (4)$$

Where  $\alpha$  and  $\beta$  are the soft-core parameters with  $\alpha=1.0$  and  $\beta=0.03$ .

$W(z, t)$  is the interaction with the external laser fields, which is

$$W(z, t) = \left( 1 + \frac{m_e}{2m_p + m_e} \right) z (E_1(t) + E_2(t - \Delta t)). \quad (5)$$

Here  $E_1(t)$  and  $E_2(t-\Delta t)$  stand for electric components of the dissociation control (THz or MIR) and UV laser fields adopted in the simulation, respectively. And  $\Delta t$  is the time delay between the two pulses. The total length of the two pulses is different, so  $\Delta t$  is defined as the difference in the on-set between the two electric fields. When the on-set of the dissociation control pulse is ahead,  $\Delta t$  is positive, otherwise, negative.

The time dependent electric fields of the dissociation control and UV pulses can be defined by the vector potentials  $A_1(t) = -E_{10}/\omega_1 \sin(\pi t/T_1)^2 \cos(\omega_1 t)$  and  $A_2(t) = -E_{20}/\omega_2 \sin(\pi t/T_2)^2 \cos(\omega_0 t + \phi)$ , then the electric components of the two fields can be obtained by  $E_{1/2}(t) =$

$-\partial A_{1/2}(t)/\partial t$  [29]. Here  $E_{10/20}$  is the peak intensity,  $T_{1/2}$  is the duration and  $\omega_{1/2}$  is the frequency of the THz (MIR)/UV pulse. And  $\phi$  is the carrier-envelope phase (CEP) of the UV laser pulse. The total simulation time is defined by  $t_{end}$ , which can be longer than the duration of the dissociation control pulse. For time beyond, the electric field is set to be zero.

For  $H_2^+$ , the two dissociation channels are defined as

$$P_{\pm} = \int_{5.7}^{R_{max}} \int_{\pm R/2.0-5.0}^{\pm R/2.0+5.0} dz |\varphi(z, R; t_{end})|^2. \quad (6)$$

Here  $R_{max}$  corresponds to the boundary of the  $R$  axis and  $\varphi(z, R; t_{end})$  is the final wave function of the system. In the simulation,  $t_{end}$  is taken at 93.4 fs after the on-set of the UV pulse, when  $P_{\pm}$ , the probabilities of the electron being localized on one of the nuclei (left - or right +), are stable. In the calculation, we set the dissociation asymmetry parameter as  $A = (P_+ - P_-)/(P_+ + P_-)$ .

For the triatomic molecular ion  $H_3^{2+}$ , the three dissociation channels, i.e., the electron localization probabilities of the left, middle and right protons are defined as

$$P_L = \int_{7.2}^{R_{max}} \int_{-(R+7.3)/1.45}^{-(R-7.2)/4.0} dz |\varphi(R, z; t_{end})|^2$$

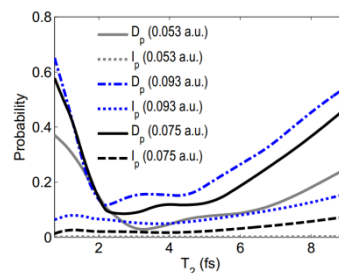
$$P_M = \int_{7.2}^{R_{max}} \int_{-(R-7.2)/4.0}^{(R-7.2)/4.0} dz |\varphi(R, z; t_{end})|^2$$

$$P_R = \int_{7.2}^{R_{max}} \int_{(R-7.2)/4.0}^{(R+7.3)/1.45} dz |\varphi(R, z; t_{end})|^2. \quad (7)$$

And the electron localization ratios of the dissociation states of these three protons of  $H_3^{2+}$  can be written as  $L_{L/M/R} = P_{L/M/R}/(P_L + P_M + P_R)$ .

## 3. Results and discussion

### 3.1 Pulse duration dependence in the photodissociation of $H_2^+$



**Figure 1:** Dissociation and ionization probabilities,  $D_p$  and  $I_p$ , as functions of duration  $T_2$  of the interaction 228 nm laser pulse. The peak electric field amplitudes of the UV pulse are 0.053, 0.075, and 0.093 a.u., respectively. The CEP of the pulse is 0.0.

A single short few-cycle UV pulse with a central wavelength of 228 nm is used to excite the electron wave packets of the initial ground  $1s\sigma_g$  state of  $H_2^+$  onto the first dissociative  $2p\sigma_u$  state. The total dissociation ratio  $D_p$  ( $D_p = \int_{5.7}^{R_{max}} dR \int_{-R/2.0-5.0}^{R/2.0+5.0} dz |\varphi(z, R; t_{end})|^2$ ) and the ionization probability  $I_p$  ( $I_p = 1 - E_{sr}$ , here  $E_{sr} = \int_{0.0}^{R_{max}} dR \int_{-z_{max}}^{z_{max}} |\varphi(R, z; t_{end})|^2$  is the electron survival probability) of  $H_2^+$  versus  $T_2$ , the duration of the interaction 228 nm laser pulse, are depicted in Figure 1. The duration of the pulse is not shorter than roughly one cycle, otherwise, the requirement  $\int E_2(t) dt = 0.0$  will be violated [30]. The peak electric field