RAPID COMMUNICATION

Electron localization of linear symmetric molecular ion H_3^{2+}*

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(Received 11 September 2016; revised manuscript received 24 October 2016; published online 29 November 2016)

Electron localization in the dissociation of the symmetric linear molecular ion H_3^{2+} is investigated. The numerical simulation shows that the electron localization distribution is dependent on the central frequency and peak electric field amplitude of the external ultrashort ultraviolet laser pulse. When the electrons of the ground state are excited onto the $2p\sigma^2\Sigma_u^+$ by a one-photon process, most electrons of the dissociation states are localized at the protons on both sides symmetrically. Almost no electron is stabilized at the middle proton due to the odd symmetry of the wave function. With the increase of the frequency of the external ultraviolet laser pulse, the electron localization ratio of the middle proton increases, for more electrons of the ground state are excited onto the higher $3p\sigma^2\Sigma_u^+$ state. 50.9% electrons of all the dissociation events can be captured by the middle Coulomb potential well through optimizing the central frequency and peak electric field amplitude of the ultraviolet laser pulse. Besides, a direct current (DC) electric field can be utilized to control the electron motions of the dissociation states after the excitation of an ultraviolet laser pulse, and 68.8% electrons of the dissociation states can be controlled into the middle proton.

Keywords: dissociation localization, time-dependent Schrödinger equation, Coulomb potential, ultraviolet laser pulse

PACS: 32.80.Rm, 33.80.Rv, 42.50.Hz, 42.65.Ky **DOI:** 10.1088/1674-1056/26/1/013203

1. Introduction

Coherent controls of electrons and fragments in chemical reactions and photoelectron processes have attracted a great deal of interest. One of the main goals is to find a way to selectively break and form molecular bonds in photochemical reactions.[1–3] For searching for the underlying mechanism in realizing electron localization control in the dissociation process, several solution routes have been proposed, which include 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] the superposition of the $2p\pi_g$ and $2p\pi_u$ states,[6] etc. In addition, the other quantum coupled equations[7–9] or laser-induced Stark shift effect[10–12] have also been used to reveal the dissociation control mechanism.

As is well known, the linear molecule in 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 interaction.[13] 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.[14] Furthermore, the collision between H^+ and H_2^+ or the dissociative ionization of H_3^+ can obtain H_3^{2+} too.[15]

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 main goal of this paper is to enhance the electron localization ratio of the dissociation states of the middle proton. 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 ultrashort ultraviolet (UV) laser pulse. When the central frequency of the UV laser pulse is 0.2 a.u., about 31.8% electrons of the ground $1s\sigma^2\Sigma_g^+$ state are excited into the exciting $2p\sigma^2\Sigma_u^+$ state through a one-photon process. There exists a symmetric electron localization distribution, as a result of the symmetric distribution of the Coulomb potential wells of the linear molecular ion H_3^{2+}. The most electrons of the dissociation states are stabilized at the protons on both sides, and almost no electron is localized at the middle proton due to the odd symmetry of the wave function of the $2p\sigma^2\Sigma_u^+$ state. With the increase of the central frequency of the UV laser pulse, more electrons of the ground state are excited onto the higher $3p\sigma^2\Sigma_u^+$ state by a three-photon process. 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 a UV laser pulse. The symmetric 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 in the direction opposite to the dc electric field force, and are captured by the

*Project supported by the National Natural Science Foundation of China (Grant Nos. 11127901, 61521093, 11134010, 11227902, 11222439, and 11274325) and the National Basic Research Program of China (Grant No. 2011CB808103).

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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.

2. Simulation model

A reduced-dimensional model for the symmetric linear H_3^{2+} molecular ion is utilized in the calculation. The molecular axis is assumed to be parallel to the polarization direction of the UV laser field. The middle proton P_1 is set to be in the center of the coordinate system. The inter-nuclear distances from P_3 and P_2 to P_1 are $R_1 = R_2 = R/2$. In other words, the UV laser pulse is assumed to have no effect on the motions of the protons. Here P_2 and P_3 are the protons located on each side of P_1. The R is the relative inter-nuclear distance between P_2 and P_3, and more details can be found in Fig. 1. Then we can adopt the one-dimensional non-Born–Oppenheimer time-dependent Schrödinger equation (TDSE) to conduct the simulation. The corresponding TDSE can be written as ($e = \hbar = 1.0$ in atomic unit (a.u.), which are used throughout the paper unless otherwise stated)[16–18]

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

where $T(R,z)$ is the field-free Hamiltonian of the system, $V_0(R,z)$ refers to the soft-core Coulomb interaction, $W(z,t)$ indicates the interaction of the particle with the external laser pulse and z represents the electronic coordinate with respect to the center of the coordinate system.

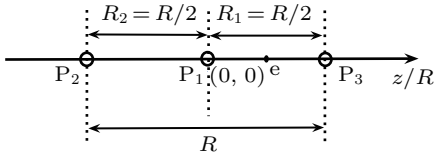


Fig. 1. Geometrical setting for the symmetric linear H_3^{2+} molecular ion along the z axis. The middle proton P_1 is stabilized in the center of the coordinates. The inter-nuclear distances from P_3 and P_2 to P_1 are $R_1 = R_2 = R/2$, where R is the relative inter-nuclear distance between the protons of P_2 and P_3.

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

$$T(R,z) = -\frac{1}{m_\mathrm{p}}\frac{\partial^2}{\partial R^2} - \left(\frac{2m_\mathrm{p}+m_\mathrm{e}}{4m_\mathrm{p}m_\mathrm{e}}\right)\frac{\partial^2}{\partial z^2}, \quad (2)$$

then the Coulomb potential of the system can be expressed as[19]

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

Here m_e and m_p are the electron mass and proton mass ($m_\mathrm{e} = 1.0$, $m_\mathrm{p} = 1837.0$), respectively. The soft-core parameters here are $\alpha = 1.0$, and $\beta = 0.03$.

The interaction of the system with the external laser field can be described as

$$W(z,t) = \left(1 + \frac{m_\mathrm{e}}{2m_\mathrm{p}+m_\mathrm{e}}\right) zE_\mathrm{UV}(t). \quad (4)$$

Here $E_\mathrm{UV}(t)$ refers to the electric component of the UV laser field.

The time dependent electric field component of the UV pulse is defined as $E_\mathrm{UV} = E_0 \sin(\pi t/T)^2 \sin(\omega t)$. Here E_0 is the peak electric field amplitude in atomic units, T is the pulse duration, and ω is the central frequency of the UV pulse. The three dissociation channels (see Fig. 2), i.e., the electron localization probabilities of the left, middle, and right protons are defined, respectively, as

$$P_\mathrm{L} = \int_{7.2}^{R_\mathrm{max}} \mathrm{d}R \int_{-(R+7.3)/1.45}^{-(R-7.2)/4.0} \mathrm{d}z\,|\varphi(R,z;t_\mathrm{end})|^2,$$
$$P_\mathrm{M} = \int_{7.2}^{R_\mathrm{max}} \mathrm{d}R \int_{-(R-7.2)/4.0}^{(R-7.2)/4.0} \mathrm{d}z\,|\varphi(R,z;t_\mathrm{end})|^2,$$
$$P_\mathrm{R} = \int_{7.2}^{R_\mathrm{max}} \mathrm{d}R \int_{(R-7.2)/4.0}^{(R+7.3)/1.45} \mathrm{d}z\,|\varphi(R,z;t_\mathrm{end})|^2. \quad (5)$$

Here R_max corresponds to the boundary range of the R axis, and $\varphi(R,z;t_\mathrm{end})$ is the final wave function of the system. In the simulation, t_end is taken as 92.6 fs after the on-set of the UV pulse, when the probabilities with which the electron are localized, respectively, on the three protons (left P_L, middle P_M, and right P_R), are all stable. The electron localization ratios of the dissociation states of these three protons are set to be $L_\mathrm{L/M/R} = P_\mathrm{L/M/R}/(P_\mathrm{L}+P_\mathrm{M}+P_\mathrm{R})$, respectively.

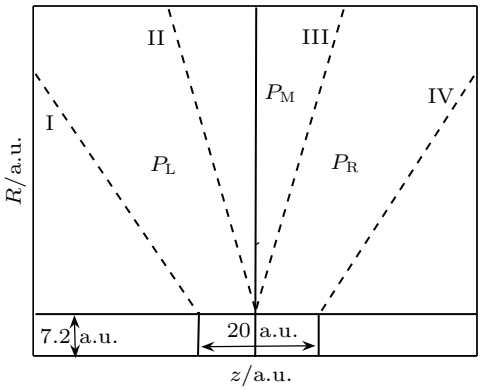


Fig. 2. Configuration space regions associated with different dissociation channels. The four dotted curves marked with I, II, III, and IV can be expressed as $R = -1.45z - 7.3$, $R = -4z + 7.2$, $R = 4z + 7.2$, and $R = 1.45z - 7.3$, respectively.

3. Simulation results and discussion

In the simulation, a UV pulse with an intensity of 1.3×10^{14} W/cm^2 and a pulse duration of 10.6 fs is used to excite the electron wave packet onto the dissociative states. Figure 3(a) shows the plots of electron localization probabilities $P_\mathrm{L/M/R}$ versus central frequency ω of the UV laser pulse for different localization ratios $L_\mathrm{L/M/R}$ of the three protons. From this

figure one can find that there exists a symmetric electron localization distribution with $P_L = P_R$ due to the symmetric distribution of the Coulomb potential well of the linear molecular ion H_3^{2+}. The electron localization probabilities and localization ratios of these three protons are all dependent on ω. When the central frequency is $\omega = 0.2$ a.u., the central wavelength of the UV laser pulse is 228 nm. The electron localization probabilities of these three protons are $P_L = P_R = 0.1584$, and $P_M = 0.00095$, respectively. Most electrons of the dissociation states are stabilized at the protons on both sides as shown in Fig. 4(a). When the central frequency of the UV laser pulse is 0.2 a.u., about 31.8% electrons of the ground $1s\sigma^2\Sigma_g^+$ state are excited onto the exciting $2p\sigma^2\Sigma_u^+$ state through a one-photon process, see Fig. 3(b).[20] For the electrons of the $2p\sigma^2\Sigma_u^+$ state, most of them are stabilized at the protons on both sides, and almost no electron is localized at the middle proton due to the odd symmetry of the wave function, which can be seen from Fig. 4(c). At the end of the simulation, the electron localization ratios of the dissociation states of these three protons are $L_L = L_R = 0.4985$, and $L_M = 0.003$, respectively. Only 0.3% electrons of the dissociation states are localized at the middle proton.

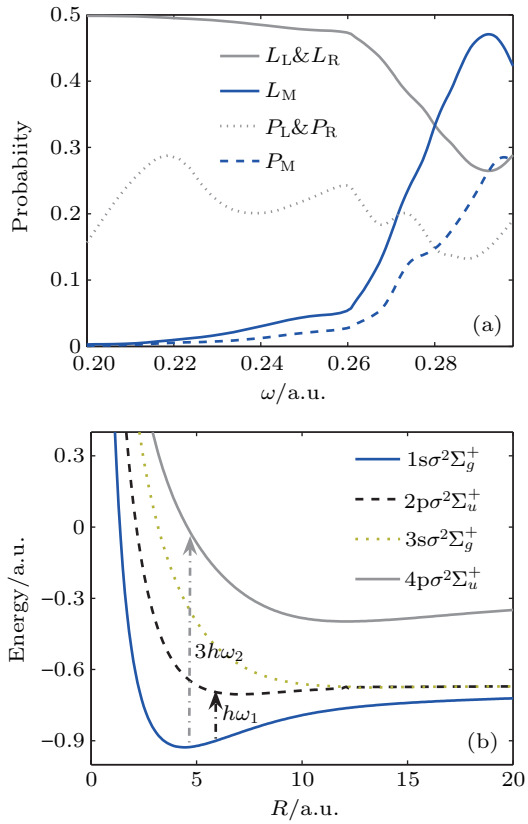


Fig. 3. (color online) (a) Variations of electron localization probabilities $P_{L/M/R}$ with central frequency ω of the UV laser pulse for different localization ratios $L_{L/M/R} = P_{L/M/R}/(P_L + P_M + P_R)$ of the three protons, where the UV laser pulse intensity is 1.3×10^{14} W/cm^2. (b) Variations of lowest four electronic energy levels of field-free linear symmetric molecular ion H_3^{2+} with R.

With the increase of ω, more electrons of the dissociation states are captured by the middle proton. For example, when the central frequency is $\omega = 0.292$ a.u., the electron localization probabilities of these three protons are $P_L = P_R = 0.1458$, and $P_M = 0.2603$, respectively, which can be seen from Fig. 4(b). The 47.2% electrons of the dissociation states are stabilized at the middle proton at the end of the simulation. When the central frequency of the UV laser pulse is $\omega = 0.292$ a.u., some electrons of the ground state $1s\sigma^2\Sigma_g^+$ state are excited onto the higher $3p\sigma^2\Sigma_u^+$ state through a three-photon process (see Fig. 3(b)). Electrons of the $3p\sigma^2\Sigma_u^+$ state can be captured by the middle proton, because the wave function includes two peaks near $z = 0.0$a.u. as shown in Fig. 4(d).

When the central frequency of the UV laser pulse is $\omega > 0.292$ a.u., the electron localization ratio of the middle proton decreases due to the decrease of the electron localization probability of the $3p\sigma^2\Sigma_u^+$ state.

From Figs. 4(a) and 44(b) one can find that the electron localization starts from about $R = 7.2$ a.u. Thus we use $R \geq 7.2$ a.u. in the definition of $P_{L/M/R}$, see Eq. (5).

Figure 5 depicts the plots of electron localization probabilities $P_{L/M/R}$ versus peak electric field amplitude E_0 of the UV laser pulse for different localization ratios $L_{L/M/R}$ of the three protons. The central frequency of the UV laser pulse is 0.292 a.u.. When E_0 is low, most electrons of the dissociation states are localized at the protons on both sides. For example, when the peak electric field amplitude of the UV laser pulse is $E_0 = 0.007$ a.u., $P_L = P_R = 0.198$, and $P_M = 0.0036$. The electron localization ratios of the left and right protons are $L_L = L_R = 0.4955$, only 0.9% electrons of the dissociation states are stabilized at the middle proton which is because when the peak intensity of the UV pulse is low, the one-photon process is dominant. The electrons of the ground state can be excited only onto the exciting $2p\sigma^2\Sigma_u^+$ state through a one-photon process. For the electrons of the $2p\sigma^2\Sigma_u^+$ state, most of them are stabilized at the protons on both sides, and almost no electron is localized at the middle proton due to the odd symmetry of the wave function. With the increase of E_0, more electrons are localized at the middle proton, which is because when the central frequency of the UV laser pulse is 0.292 a.u., the electrons of the ground state can be excited onto the higher $3p\sigma^2\Sigma_u^+$ state through a three-photon process. The electrons of the $3p\sigma^2\Sigma_u^+$ state can be captured by the middle potential well. The excitation ratio of the three-photon process is dependent on the peak electric field amplitude E_0 of the UV laser pulse seriously. For example, when the peak electric field amplitude is 0.0475 a.u., the electron localization probabilities of these three protons are $P_L = P_R = 0.1686$, and $P_M = 0.3494$, respectively. The 50.9% electrons of all the dissociation events are stabilized at the middle proton.

With the further increase of E_0, the electron localization probabilities of these three protons all drop. More electrons are ionized and escape away.

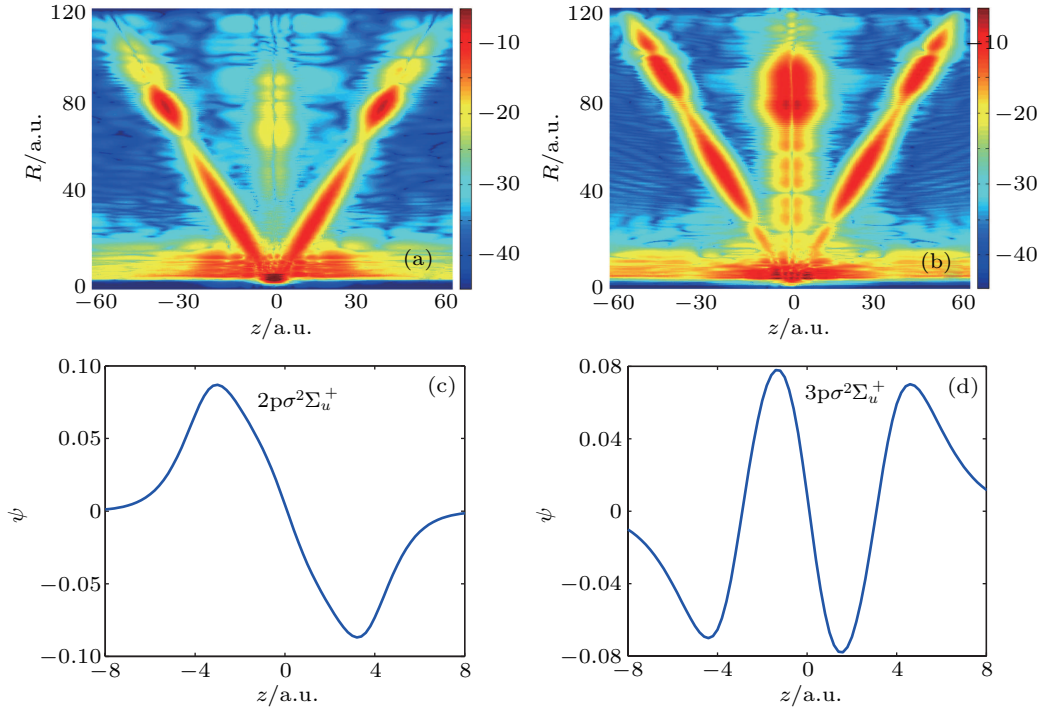


Fig. 4. (color online) Upper panels: snapshots of the common logarithm of the electron-nuclear probability density distribution taken at the end of the dissociation, with the central frequencies of the UV laser pulse being (a) 0.2 a.u. and (b) 0.292 a.u. Lower panels: the wave functions corresponding to (c) $2p\sigma^2\Sigma_u^+$ and (d) $3p\sigma^2\Sigma_u^+$ states, respectively.

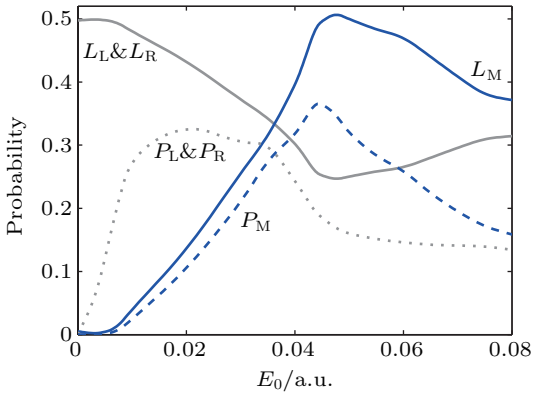


Fig. 5. (color online) Plots of electron localization probabilities $P_{L/M/R}$ versus peak electric field amplitude E_0 of the UV laser pulse for different localization ratios $L_{L/M/R} = P_{L/M/R}/(P_L + P_M + P_R)$ of the three protons. The central frequency ω of the UV laser pulse is 0.292 a.u.

The other way to enhance the electron localization ratio of the dissociation states of the middle proton is to use a DC electric field, whose polarization is assumed to be parallel to the molecular axis, to steer the electron motion after the excitation of an ultrashort UV laser pulse. For the UV pulse, the pulse duration, central laser frequency, and intensity are 10.6 fs, 0.2 a.u., and 1.3×10^{14} W/cm^2, respectively. Figure 6(a) shows the variations of the electron localization probabilities $P_{L/M/R}$ with the amplitude of the dc electric field E_{dc} for different electron localization ratios $L_{L/M/R}$ of these three protons. When E_{dc} approaches 0.0, there appears a symmetric electron distribution with $P_L = P_R$, and almost no electrons of the dissociation states are stabilized at the middle proton due to the symmetric distribution of the Coulomb potential wells of the linear symmetric molecular ion H_3^{2+} and the odd symmetry of the wave function of the $2p\sigma^2\Sigma_u^+$ state.

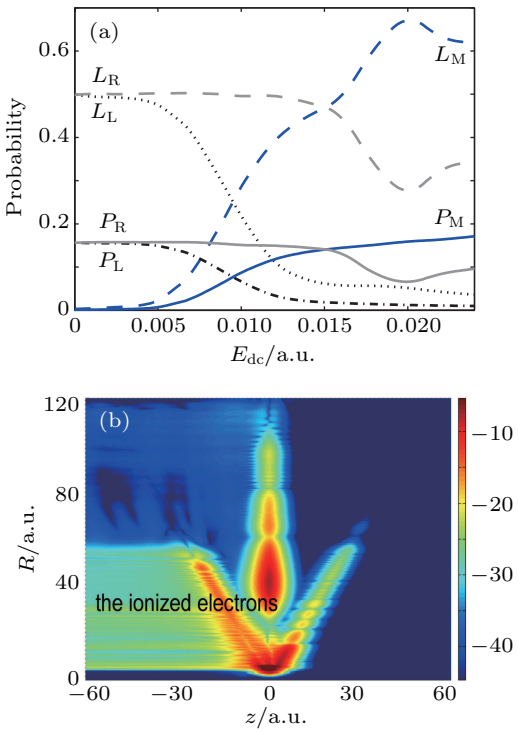


Fig. 6. (color online) (a) Plots of electron localization probabilities $P_{L/M/R}$ versus the amplitude E_{dc} of DC electric field for different localization ratios $L_{L/M/R} = P_{L/M/R}/(P_L + P_M + P_R)$ of the three protons, in which a DC electric field is utilized to steer the electron motions of the dissociation states after being excited by a UV laser pulse with a central frequency and intensity of 0.2 a.u. and 1.3×10^{14} W/cm^2, respectively. (b) Snapshot of the common logarithm of the electron-nuclear probability density distribution taken at the end of the dissociation, with the amplitude of the dc electric field being $E_{dc} = 0.02$ a.u.

With the increase of the amplitude of the dc electric field E_{dc}, the symmetric electron localization distribution is broken seriously, as a result of the dressing effect of the DC electric field. The ionized electrons escape away along the DC electric field force, see Fig. 6(b), while most of the electrons in the dissociation states, which are localized at the left proton subjected to a single UV laser pulse, move in the direction opposite to the DC electric field force, and are stabilized at the middle proton.[21] When $E_{dc} > 0.015$a.u., the electrons on the right proton start to be ionized away while the electrons of the middle proton are stabilized due to a deeper potential well. When the amplitude of the DC electric field is $E_{dc} = 0.02$ a.u., the electron localization probabilities of these three protons are $P_L = 0.0122$, $P_M = 0.1594$, and $P_R = 0.0612$, respectively, which can be seen from Fig. 6(b). The 68.8% electrons of the dissociation states are stabilized at the middle proton at the end of the simulation.

With the further increase of the amplitude of the dc electric field, the electron localization ratio of the middle proton decreases, for a further dissociation is induced.

4. Conclusions

In this work, the electron localization in the dissociation of the symmetric linear molecular ion H_3^{2+} is investigated. The numerical simulation shows that the electron localization ratio of the middle proton is dependent on the central frequency and peak electric field amplitude of the external UV laser pulse. When the electrons of the ground state are excited onto the $2p\sigma^2\Sigma_u^+$ by a one-photon process, almost no electron is stabilized at the middle proton due to the odd symmetry of the wave function. With the increase of the central frequency of the UV laser pulse, more electrons of the dissociation states are stabilized at the middle proton, because more electrons of the ground state are excited onto the higher $3p\sigma^2\Sigma_u^+$ state through a three-photon process. The electron localization ratio of the middle proton can be raised to 50.9% by optimizing the central frequency and peak electric field amplitude of the UV pulse. Besides, a DC electric field can be utilized to control the electron motions of the dissociation states after being excited by an ultrashort UV laser pulse. The symmetric electron localization distribution is broken seriously due to the dressing effect of the DC electric field. The electrons of the dissociation states, which are localized at the potential well of one side, move in the direction opposite to the DC electric field force and are stabilized at the middle proton. As the amplitude of the DC electric field changes, 68.8% electrons of all the dissociative events can be controlled onto the middle proton.

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