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Ionization Channels of the Molecular Ion H_2^+ in Intense Laser Field *

MIAO Xiang-Yang(苗向阳)**, SHI Hao-Ting(施昊霆)

College of Physics and Information Engineering, Shanxi Normal University, Linfen 041004

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Ionization channels of the molecular ion H_2^+ for various initial vibrational states in intense laser field (80 fs, 800 nm, $I = 6.8 \times 10^{13}$ W/cm^2) are theoretically investigated by numerically solving the time-dependent Schrödinger equation. The results confirm that the channels largely depend on the selection of initial vibrational states by analyzing the variations of peak locations in the nuclear initial kinetic-energy-release spectra. Furthermore, the selection of the ionization channels is sensitive to the wavelength of the laser pulse. In addition, time-dependent competition between direct multi-photon ionization and charge-resonance-enhanced ionization are is discussed.

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In recent years, much attention has been paid to the behavior of atoms in an intense laser field, for example, Wu and Yang have investigated the atomic coherence properties produced by an ultrafast laser pulse,[1,2] Shao *et al.* have made a theoretical exploration of the laser-parameter effects on the high-order harmonic generation from atoms.[3] Nowadays, molecules, especially the hydrogen molecule and its molecular ion, have been the simplest models to be employed to reveal many more physical phenomena such as bond-softening (BS),[4,5] bond-hardening (BH),[6] above-threshold dissociation,[7,8] above-threshold ionization[9] and charge-resonance-enhanced ionization (CREI).[10] Among these phenomena, the CREI at so-called critical internuclear distances is of special interest.[11,12] The energies of the protons from these processes are ordinarily located in a range from 0 to 10 eV, which has been well studied.[13,14] However, even higher energy peaks in the kinetic energy released (KER) spectrum of protons have been observed by Niikura *et al.*[15] To explain this phenomenon, Staudte *et al.*[16] have considered two possible mechanisms of the higher energy peaks which may be induced by a multi-rescattering process of the first ionized electron or a direct multi-photon ionization (DMPI) from the molecular ion, and confirmed that the DMPI process is more effective for the high kinetic energy region than the multi-rescattering process. Thus, in the intense laser field, the electron of H_2^+ can be mainly ionized via DMPI and CREI channels.

Vafaee *et al.* have shown explicitly that the transition of the wave packet from the coupling states $1s\sigma_g$ and $2p\sigma_u$ to the ionization state is not a direct transition, but takes place through other intermediate states when the CREI occurs.[17] In this situation, the kinetic energy of protons is equal to the extra energy obtained from the intermediate states plus $1/R$.[18,19] The extra energy obtained after the intermediate states process is known as the initial kinetic energy (IKE) of protons. It is clear that the intermediate states process cannot occur in the DMPI channel. Thus the value of the IKE is a mirror to decide which ionization channels of H_2^+ exposed in a strong field can be selected: for the case that the value of nuclear IKE cannot be ignored compared with that of the kinetic energy of protons, the nuclear wave packet may first be excited to the intermediate state from the dissociative state, and then move along the state till CREI occurs at the critical internuclear distance. Namely, the intermediate states process is prominent; for the other case that the value of the nuclear IKE can be ignored, the DMPI process that the wave packet transits directly to the ionization state or the CREI process that the wave packet transits directly from the coupling states $1s\sigma_g$ and $2p\sigma_u$ to the ionization state takes place.

In this Letter, the selection of the ionization channels of H_2^+ in an intense laser field and the intermediate state process when the CREI takes place at various initial vibrational states are discussed in detail by analyzing the corresponding nuclear initial kinetic energy released (IKER) spectra. In addition, the influences of the laser wavelength and the full-width at half-maximum (FWHM) on the ionization channels are investigated. Incidentally, the time-dependent competitions between DMPI and CREI at $v = 1$ are briefly discussed.

In principle, an accurate theoretical description of these dynamics needs to explicitly integrate the time-dependent Schrödinger equation (TDSE). Plenty of theoretical investigations have used the Born–Oppenheimer (BO) approximation,[20,21] which sepa-

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**Corresponding author. Email: sxxymiao@126.com

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rates the nuclear motion from the electronic motion. It is hard to obtain exact results since the intense laser field may influence the Coulomb potential of molecule ions. Thus, a full-dimensional simulation that simultaneously considers the nuclear and electronic dynamics is desired for more accuracy. However, the full-dimensional solution of the TDSE without use of the BO approximation is beyond our current ability, so we must use physical reasoning and intuition to reduce the dimensionality to a manageable scale that also retains the essential physics of the problem.[11] Here we employ a one-dimensional (1D) model with a soft-core Coulomb potential and use the non-BO approximation in order to simulate the nuclear IKER spectra of H_2^+. All calculations have been performed with our parallel quantum wave packet computer code LZH-DICP.[22] Throughout this study, we use atomic units unless stated specifically.

When the linearly polarized laser field is considered along with the molecular axis, in the dipole approximation and in the length gauge, the Hamiltonian of 1D model reads

$$H(R,z,t) = -\frac{1}{m_p}\frac{\partial^2}{\partial R^2} - \frac{1}{2}\frac{\partial^2}{\partial z^2} + \frac{1}{R} - \frac{1}{\sqrt{(z-R/2)^2+1}} - \frac{1}{\sqrt{(z+R/2)^2+1}} + kzf(t)E_0\cos(\omega t), \quad (1)$$

where m_p is the mass of the nucleus, R is the internuclear distance, z is the electron coordinate with respect to the nuclear center of mass, $k = 1 + \frac{1}{2m_p+1}$, ω is the laser frequency, and E_0 is the electric field amplitude, $f(t)$ is a Gaussian pulse envelope of the form

$$f(t) = \exp\Big(-4\ln 2\frac{t^2}{\tau^2}\Big), \quad (2)$$

in the present work, τ is the FWHM.

The initial vibrational wave packets of the molecular ion can be constructed by diagonalizing the field-free (discretized) Hamiltonian.[11]

The sine basis functions are employed to define a discrete-variable-representation (DVR) for the translational coordinate R and z,[23–25]

$$\langle x_i|n\rangle = \sqrt{\frac{2}{L}}\sin\Big(\frac{n\pi x_i'}{L}\Big) = \sqrt{\frac{2}{L}}\sin\Big(\frac{in\pi}{N+1}\Big), \quad (3)$$

where $L = x_{\max} - x_{\min}$, $x_i' = x_i - x_{\min} = i\Delta x$ with $i = 1, 2, \ldots, N$; and $\Delta x = L/(N+1)$. The corresponding DVR basis is defined as

$$\langle \overline{x_i}|n\rangle = \sqrt{\Delta x}\langle x_i|n\rangle. \quad (4)$$

The time-dependent wave function is advanced using the standard second-order split operator method,

$$\psi(R,z,t+\delta t) = e^{-iT\delta t/2}e^{-iV\delta t}e^{-iT\delta t/2}\psi(R,z,t) + O(\delta t^3), \quad (5)$$

where T is the kinetic energy operator as in Eq. (1), and V is the interaction potential taking all the potential energy of the system plus a purely imaginary term to produce an absorbing boundary.

The numerical parameters of the converged results for H_2^+ are as follows: the grids cover the ranges from 0 to 30 in R and from -45 to 45 in z, with 300 and 226 points, respectively. The time step δt, which is associated with the nuclear motion, is set to be 0.2. The calculations are performed under a condition of 800 nm, 80 fs (FWHM) laser pulse. The flux operator and virtual detect methods[25] are adopted to obtain the probabilities and energies of the IKER spectrum, and a binning procedure is necessary to derive the IKER spectrum across the whole interaction time of the laser pulse.

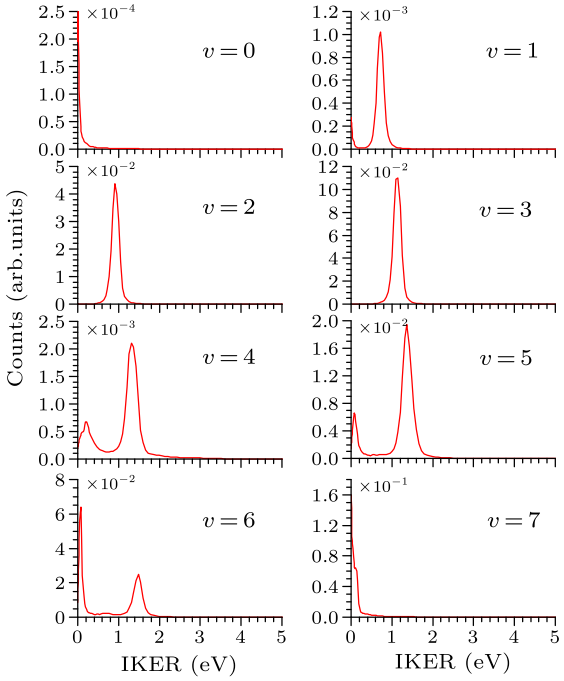


Fig. 1. The nuclear IKER spectra of H_2^+ for initial vibrational states from $v = 0$ to $v = 7$. The peak intensity of the laser pulse is 6.8×10^{13} W/cm^2, FWHM is 80 fs, wavelength is 800 nm.

In detail, the selection of the ionization channels of H_2^+ in intense laser field at various initial vibrational states is investigated by simulating the nuclear IKER spectra from $v = 0$ to $v = 7$ in Fig. 1. The laser peak intensity is 6.8×10^{13} W/cm^2, FWHM is 80 fs, wavelength is 800 nm. It is clear that the IKER peaks of H_2^+ shift toward high energies as the vibrational levels increase from $v = 1$ to $v = 5$ while the corresponding peak energy at $v = 0$ is very close to 0 eV. However, it is different from the cases in higher vibrational levels from $v = 6$ to $v = 7$, in which the main peak energies of the spectra are approximately equal to 0 eV. The results show that the extra energies of nuclei obtained from the intermediate states

can be ignored when the initial vibrational states are chosen as extremal ones ($\upsilon = 0$, 6, 7). In addition, it is worth noting that there are double peak structures in the spectra at $\upsilon = 1$, 4, 5 and 6, which may correspond to two ionization channels. Thus we expect that the ionization channels are different when the initial vibrational states are selected as extremal ones ($\upsilon = 0$, 6, 7) and the others (from $\upsilon = 1$ to $\upsilon = 5$), respectively. As we all know, the DMPI occurs at short internuclear distances, especially at near equilibrium distance, while the CREI takes place at larger internuclear distances.[18] Because the intermediate state process does not occur at $\upsilon = 0$, 6, 7 and even higher vibrational states, the scope of R is originally larger, the DMPI process may occur at $\upsilon = 0$ and the CREI may take place through the direct transition from the dissociative state to the ionization state at $\upsilon = 6$ and $\upsilon = 7$ compared with the ionization process from $\upsilon = 1$ to $\upsilon = 5$, where the transition from the coupling states $1s\sigma_g$ and $2p\sigma_u$ to the ionization state is not a direct transition, but takes place through other intermediate states.

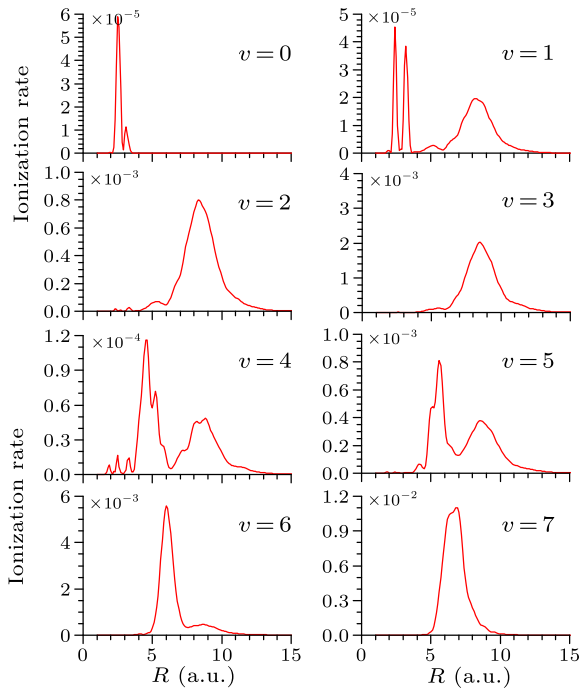


Fig. 2. The R-dependent ionization rates of H_2^+ for the states from $\upsilon = 0$ to $\upsilon = 7$, respectively. The laser conditions are the same as those in Fig. 1.

For the sake of testing the correctness of the inference proposed above, the R-dependent ionization rates of H_2^+ for various states from $\upsilon = 0$ to $\upsilon = 7$ are calculated in Fig. 2. It indicates that the molecular ions ionize in a range of internuclear distances. It is more importantly concluded that the ionization channels of H_2^+ exposed to intense laser pulses is the DMPI at $\upsilon = 0$, where the molecular ion H_2^+ mainly ionizes at $R = 2$ a.u. while others are all the CREI at states from $\upsilon = 1$ to $\upsilon = 7$. However, the CREI processes taking place from $\upsilon = 1$ to $\upsilon = 5$ are distint from those occurring at $\upsilon = 6$ and $\upsilon = 7$. Attention should also be paid to the fact that two typical peaks appear in the results of Fig. 2 at $\upsilon = 1$, 4, 5 and 6, which can explain very well why the double peak structures of the spectra emerge at corresponding states in Fig. 1 and two ionization channels simultaneously exist only at $\upsilon = 1$. Based on the above analyses, the conclusion that the guess is correct and reasonable is drawn. More than anything is that the ionization channels of H_2^+ at various states can be confirmed by depicting the nuclear IKER spectra according to the analysis of Figs. 1 and 2.

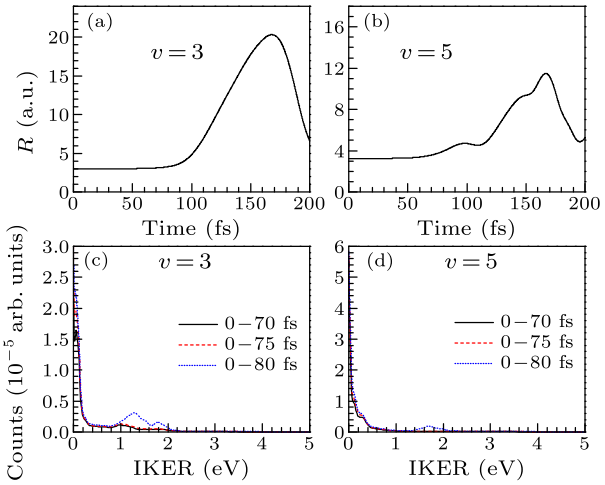


Fig. 3. The time-dependent average internuclear distances and the time-dependent IKER spectra of H_2^+ at $\upsilon = 3$ and $\upsilon = 5$.

In order to clarify qualitatively why the spectrum peaks can appear in the results in Fig. 1, the classical theory method can be adopted. The value of peak energy in the IKER spectrum depends largely on three factors: R_d, R_c and E_d (the kinetic energy at the internuclear distance R_d). R_d is the internuclear distance at which the transition of the nuclear wave packet occurs from the dissociative state to the intermediate states. R_c is the critical internuclear distance where the CREI takes place. It is understandable that for the same vibrational state, the larger the R_d and the difference of the R_c and R_d are, the larger the energy E_d and the energy E_i that the nuclear wave packet gains along the intermediate state are, respectively, so the value of peak energy in the IKER spectrum equals to the E_d plus the E_i. It is distinctly pivotal to determine the locations of the R_d and the R_c for various states. Very fortunately, both of the internuclear distances can be confirmed by calculating the space-dependent ionization rate. In Fig. 2, the location of the R where the ionization rate is exactly maximal is R_c. However, we guess reasonably that the R_d is also the special internuclear distance where the nuclear wave packet

first ionizes through the CREI channel process rather than the DMPI one. With the purpose of proving the reasonableness of the guess about the location of the R_d, the time-dependent average internuclear distances $R(t)$ and the time-dependent IKER spectra at two arbitrary states, here the $v = 3$ and $v = 5$ are shown in Fig. 3, respectively. In Figs. 3(a) and 3(b), due to the intense laser pulse being periodic, the change of $R(t)$ can be oscillatory. In Figs. 3(c) and 3(d), the peak just obviously occurs when the time is 80 fs at both states, indicating that the nuclear wave packet reaches the intermediate state from the dissociative state and starts to achieve the IKE at R_d at this moment, and then, the R_d located at 4 a.u. in Figs. 3(a) and 3(b) at the moment 80 fs no matter whether the state is $v = 3$ or $v = 5$, matches well with the internuclear distance where the ionization just takes place through the CREI process at $v = 3$ and $v = 5$ in Fig. 2. Similar results can appear at other states, which are not shown here, demonstrating that the guess is available.

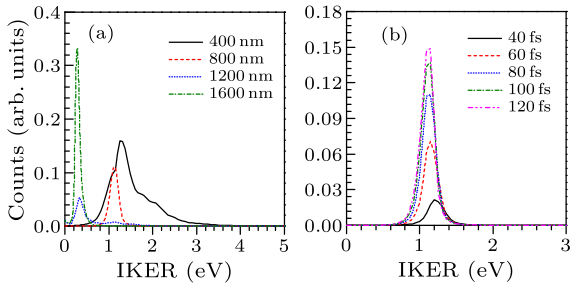


Fig. 4. The nuclear IKER spectra of H_2^+ for (a) various laser wavelengths and (b) the pulse FWHM for the $v = 3$, respectively. The pulse FWHM is 80 fs in (a) and the laser wavelength is 800 nm in (b).

Figure 2 shows that the R_d is almost same (4 a.u.) from $v = 1$ to $v = 5$ while they are 4.5 a.u. at $v = 6$ and $v = 7$. For the R_c, the locations are all about at 9 a.u. from $v = 1$ to $v = 5$ while they are at 6 a.u. and 7 a.u. at $v = 6$ and $v = 7$, respectively, so the energy E_i should be same at the states from $v = 1$ to $v = 5$. However, the energy E_d becomes larger with the states increasing from $v = 1$ to $v = 5$, so the peak energies of the IKER spectra move to the higher level. However, the differences of the R_c and R_d at $v = 6$ and $v = 7$ are much smaller than those at the states from $v = 1$ to $v = 5$, leading to the fact that the energies E_i at $v = 6$ and $v = 7$ are much smaller than those at the states from $v = 1$ to $v = 5$ even if the E_d increases as the states from $v = 6$ to $v = 7$. The reason why the peak energies of IKER spectra can be ignored for the cases in vibrational levels $v = 6$ and $v = 7$ compared with other vibrational levels from $v = 1$ to $v = 5$ may be such that the values of the peak energies in the IKER spectra at those states mostly depend on the E_i rather than the E_d.

The influences of the laser parameters on the selection of the ionization channels are discussed in Figs. 4(a) and 4(b) for various laser wavelengths and pulse FWHM for the $v = 3$, respectively. In Fig. 4(a), it is obvious that the peak locations shift to low levels with the increase in the wavelength. It is more important that the spectrum peaks appearing at 1200 nm and 1600 nm are equal to 0 eV while those at 400 nm and 800 nm are relatively large, implying that the ionization channel of H_2^+ when the wavelengths are 1200 nm and 1600 nm is different from that of H_2^+ when the wavelengths are 400 nm and 800 nm according to the conclusion of Fig. 1. Thus the ionization channels of H_2^+ in an intense laser field can be controlled by changing the wavelength of the laser pulse. It is worth noting that the counts of the spectra at 1200 nm and 1600 nm are artificially enlarged 100 times so as to compare intuitively the variations of the peak locations in spectra. In Fig. 4(b), the peak moves slightly to low energy when the FWHM varies from 40 fs to 60 fs, however, the peak location is almost constant when the FWHM changes from 80 fs to 120 fs even though the peak counts are increasingly higher. It can be concluded that the peak location of the nuclear IKER is very sensitive to the wavelength of the laser pulse and the intermediate state process occurs from 80 fs to 120 fs.

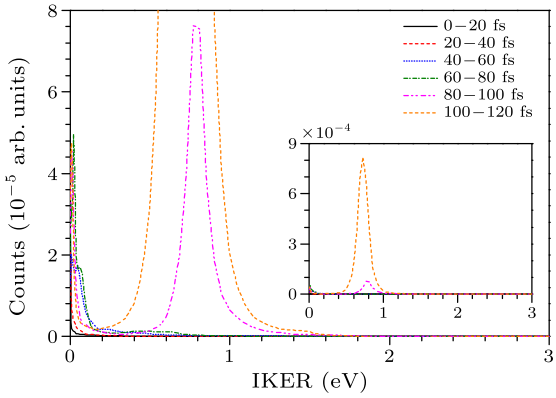


Fig. 5. The time-dependent evolution IKER spectra of H_2^+ for $v = 1$. The details of the evolution from 0 fs to 120 fs are given. The inset is the enlargement of the spectra.

Lastly, the time-dependent IKER spectra for $v = 1$ are shown in Fig. 5. The peak just occurs when the moment is 80 fs, however, the peak location is almost constant with the increase of time from 100 fs to 120 fs, so it is distinct that the intermediate state process begins at 80 fs and ends at 120 fs, and the probability of the wave packet which experiences this process increases during this time. The reason why the intermediate state process or the ionization cannot occur from 0 fs to 80 fs may be that strong charge resonance between the ground state and the dissociative state of H_2^+ appears; consequently the population of $2p\sigma_u$ becomes more than that of the $1s\sigma_g$ state occasionally[19]

or only the DMPI channel occurs in this time. The time-dependent internuclear populations of the ionization of H_2^+ are briefly discussed in Fig. 6 to verify the results in Fig. 5. Before 80 fs, it seems that the pathway of the ionization through the DMPI is opened and another pathway of the ionization via the CREI is closed; however, the pathway of the ionization through the CREI at $R = 8$ a.u. is opened and it plays a dominant role gradually from 80 fs to 120 fs.

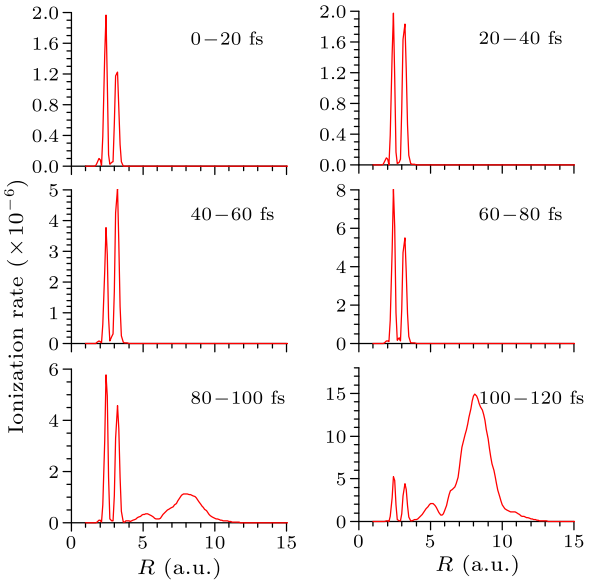


Fig. 6. The time-dependent internuclear populations of the ionization of H_2^+ at $v = 1$.

In conclusion, we have numerically solved the TDSE of H_2^+ in an intense laser field, and the selection of the ionization channels for various initial vibrational states is studied in detail by depicting the corresponding nuclear IKER spectra of H_2^+. For $v = 0$, the ionization channel is the DMPI. The CREI takes place through the direct transition from the dissociative state to the ionization state at $v = 6$ and $v = 7$. Compared with that ionization process, the transition from the coupling states $1s\sigma_g$ and $2p\sigma_u$ to the ionization state is not a direct transition, but takes place through other intermediate states during the CREI from $v = 1$ to $v = 5$. Furthermore, the intermediate state process when the CREI takes place is studied in detail by explaining the reason why the peak energy of IKER spectra varies for various states. In addition, we demonstrate that the selection of the ionization channels is sensitive to the wavelength of the pulse, so the channels can be controlled by adjusting the wavelength of the pulse. Lastly, the time-dependent competitions between DMPI and CREI are discussed. At the beginning of the laser pulse, the ground state of H_2^+ is strongly coupled with $2p\sigma_u$. From 0 fs to 80 fs, the pathway of the DMPI is opened and the corresponding probability increases while the CREI is closed. As the time increases (80–120 fs), the DMPI is gradually closed, and the CREI begins to open and is predominant.

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