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Attosecond resolution quantum dynamics between electrons and H_2^+ molecules

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The time-dependent-wave-packet method has been applied to calculate the kinetic energy distribution of H^+ ion resulting from the recollision between the electron and its parent ion $H_2^+(X^2\Sigma_g^+)$ within subfemtosecond time scale. The recollision probabilities between the electron and H_2^+ as a function of time have also been obtained. Also, an accurate quantum dynamics method has been applied to describe the motion of both the electron and the nuclear wave packets with attosecond resolution. The calculated results are in good agreement with experimental ones.

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I. INTRODUCTION

Recently, attosecond optical pulses are generated commonly by the tunnel ionization or the electron recollision method through the process of high-order harmonic generation [1–8]. Drescher *et al.* have established a detailed theoretical method in the case of atoms to study the time-resolved electron spectroscopy of atomic inner shell using attosecond extreme ultraviolet light source [4,9]. Now, much effort has been put into the study of molecules [10–13]. The fast-moving electron produced by field ionization can be accelerated to probe molecular structure. For example, Niikura *et al.* deduced the time structure and magnitude of the recollision electron wave packet by using the vibrational wave packet of H_2^+, which is proposed an entanglement method to probe the H_2^+ vibrational wave packet with subfemtosecond resolution [14]. In Niikura *et al.*'s work [14], 40 fs, 1.5×10^{14} W/cm^2 laser pulse with 800 nm wavelength is used to ionize the H_2 molecule, and the kinetic energy distribution of H^+ is measured with the laser polarization being perpendicular to the molecular axis. They predicted that the H^+ ions mainly result from the recollision between the electron and its parent ion, and the attosecond bound-state wave packet dynamics has been fully characterized in their up to date work by solving the one-dimensional (1D) time-dependent Schrödinger equation [15].

In the previous paper [16], we have carried out a three dimensions (3D) time-dependent- wave-packet calculation, i.e., electron in two dimensions and nuclei in one dimension to study the recollision between the electron and D_2^+ ion. Here, we apply the same method to calculate the time-resolved kinetic energy spectra of H^+ and the probabilities of recollision between the returning electron and its parent ion $H_2^+(X^2\Sigma_g^+)$. First, the ionization weakens the binding force between the electron and neutral H_2 molecule, then one of the two bonding electrons becomes free, and the vibrational wave of H_2^+ ion launches on its ion surface $H_2^+(X^2\Sigma_g^+)$ immediately, as shown in Fig. 1. The H_2^+ population will transfer to its excited or double ionization states. But the probability of the double ionization is very small [14]. Thus, the electronic and vibrational wave packets are correlated within the time scale of the laser oscillation.

II. THEORETICAL METHOD

The multibody problems such as the interactions between the electron and the ions in intense laser field can be studied by solving the time-dependent Schrödinger equation [17,18]. In view of the time scale, the electronic wave function becomes stationary on 0.9 fs during a field-induced transition, and it is much shorter than that of the nuclei (about 60 fs) [19]. So we write the Schrödinger equation as

$$i\hbar\frac{\partial}{\partial t}\psi_{\mathrm{I}}(R,\vec{r},t)=\left[-\frac{\hbar^2}{2\mu}\nabla^2+V_{\mathrm{I}}\right]\psi_{\mathrm{I}}(R,\vec{r},t),\qquad(1)$$

$$i\hbar\frac{\partial}{\partial t}\psi_{II}(R,t)=\left[-\frac{\hbar^2}{m_p}\frac{\partial^2}{\partial R^2}+V(R,t)\right]\psi_{II}(R,t).\qquad(2)$$

We employ a single-active-electron approach, and only one electron coordinate is included in Eq. (1). The other electron

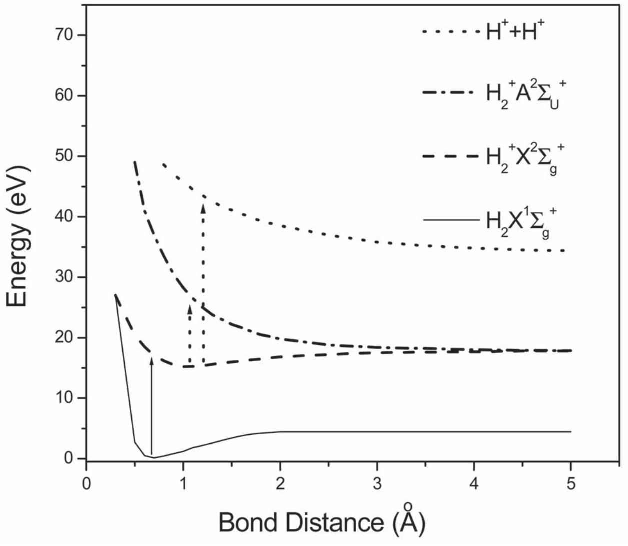

FIG. 1. The potential energy surfaces used during our calculation are shown [14].

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is the bound electron to be considered together with the nuclei. Equation (1) depicts the motion of the electron in the strong laser field, and R is the inter-nuclear distance, $\vec{r}$ is electron coordinate, the item μ is the reduced mass. Equation (2) denotes the motion of the nuclei, and $-\frac{\hbar^2}{m_p}\frac{\partial^2}{\partial R^2}$ is the kinetic energy of the nuclei with its initial wave function being the vibrational ground state of H_2.

The Schrödinger equation of the single electron and the nuclei can be calculated in cylindrical coordinate [20–22] in order to simplify our calculation. Thus, the azimuthal electron coordinate will be eliminated by symmetry [23,24]

$$i\hbar\frac{\partial}{\partial t}\psi_1(\rho,z,t) = \left[-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial\rho^2}+\frac{1}{\rho}\frac{\partial}{\partial\rho}+\frac{\partial}{\partial z^2}\right)+V_{\mathrm{I}}\right]\psi_1(\rho,z,t). \tag{3}$$

In Eq. (3), (ρ,z,t) is the cylindrical coordinate of the recollision electron, and that of the bound electron is included in the potential of the H_2^+. The item $-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial\rho^2}+\frac{1}{\rho}\frac{\partial}{\partial\rho}+\frac{\partial}{\partial z^2}\right)$ denotes the kinetic energy of the electrons, and the potential energy V_I includes several parts: $V(R,t)$, V_C and $-2\Gamma\hbar\frac{\partial^2}{\partial t^2}$, where $\Gamma=\frac{\hbar}{m_e\alpha^2c^2}$ denotes the relaxation time (m_e, α, and c denote one electron mass, fine structure constant and the speed of light, respectively). The potential $V(R,t)$ includes the interactions of the bound electron with the nuclei and the nucleus with the other nucleus in our calculation, and the item V_C being widely used in previous works [15,25] is the Coulomb interaction between the recollision electron and the nuclei

$$V_C = -\frac{1}{\sqrt{\rho^2+(z-R/2)^2}}-\frac{1}{\sqrt{\rho^2+(z+R/2)^2}}. \tag{4}$$

Because there is only one bound electron in as to the H_2^+ molecule, the correlated interaction of the electrons is not considered, except when the recollision electron is pulled back by the laser field to recollide with its parent ion. Meanwhile, due to the frictional force the electron in hydrogenlike atoms move with the constant velocity $V=\alpha C$ (α and C denote the fine structure constant and the light velocity) [26]. Kozlowski and Marciak-Kozlowska have introduced an additional item $-2\Gamma\hbar\frac{\partial^2}{\partial t^2}$ as a kind of frictional force to describe the interaction of the electron with its surrounding in atom [26]. However, in the continuum, the active electron almost does not interact with the core [6], so it is worthwhile to apply this additional item to describe the interaction between the two electrons during the very short laser pulses.

The potential energy $V(R,t)$ includes the ground state $H_2(X^1\Sigma_g^+)$, the ionic state $H_2^+(X^2\Sigma_g^+)$ and the excited state $H_2^+(A^2\Sigma_u^+)$

$$V(R,t)=\begin{pmatrix} V_X & W_{X'X} & 0 & \cdot & \cdot & \cdot & \cdot & 0 \\ W_{XX'} & V_{X'} & W_{IX'} & \cdot & \cdot & \cdot & \cdot & W_{IX'} \\ 0 & W_{X'I} & V_I+E_{I,1} & 0 & \cdot & \cdot & \cdot & 0 \\ \cdot & \cdot & 0 & V_I+E_{I,2} & 0 & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & 0 & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 0 \\ 0 & W_{X'I} & 0 & 0 & \cdot & \cdot & 0 & V_I+E_{I,n} \end{pmatrix}. \tag{5}$$

Here, V_X and $V_{X'}$ denote H_2 $(X^1\Sigma_g^+)$ and H_2^+ $(X^2\Sigma_g^+)$ states, respectively. $W_{ij}=\mu_{ij}E(t)(i,j=X,X',I;i\neq j)$ denotes the coupling between the electronic states involved with the dipole matrix elements μ_{ij} and the external field $E(t)$. The item V_I refers to the potential energy of $H_2^+(A^2\Sigma_u^+)$ state [14], and the population of H_2^+ will transfer from $X^2\Sigma_g^+$ to the excited state $A^2\Sigma_u^+$ after the recollision between the electron and its parent ion. $V_I+E_{I,n}(n=1,2,\ldots,60)$ denote the potential energies of the discrete set of continuum state $A^2\Sigma_u^+$. The energy accuracy of the discrete set of continuum states can amount to 1.6% by choosing $n=60$, and the time-dependent equation is solved with 2048 time steps per laser cycle starting from the ground state of H_2. The Coulomb interaction V_C and the correlated interaction $V_\Gamma=-2\Gamma\hbar\frac{\partial^2}{\partial t^2}$ will be added respectively to each diagonal and off-diagonal items of the continuum ionic states $H_2^+(A^2\Sigma_u^+)$, and the values of the correlated interaction can be got and added to the potential V_I before the further calculation.

The wave function of the electrons is calculated by the time-dependent Schrödinger Eq. (3) with the method of 'split-operator-Fourier' [27,28]. The time-dependent wave function is advanced using the second-order split-operator scheme

$$\psi(t+\delta t,\rho,z)=\exp\left(-\frac{iH_1}{2\hbar}\delta t\right)\exp\left(-\frac{iH_2}{\hbar}\delta t\right)\times\exp\left(-\frac{iH_1}{2\hbar}\delta t\right)\psi(t,\rho,z)+O(\delta t^3), \tag{6}$$

where

$$H_1 = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho}\frac{\partial}{\partial\rho} + \frac{\partial^2}{\partial z^2}\right),$$

$$H_2 = V_C + V(R,t) - 2\Gamma\hbar\frac{\partial^2}{\partial t^2}. \tag{7}$$

The operation $\exp\left(-\frac{iH_1}{2\hbar}\delta t\right)\psi(t,\rho,z)$ can be carried out as

$$\exp\left(-\frac{iH_1}{2\hbar}\delta t\right)\psi(t,\rho,z),$$

$$\exp\left[\frac{i\hbar\,\delta t}{4\mu}\left(\frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho}\frac{\partial}{\partial\rho}\right)\right]\exp\left(\frac{i\hbar\,\delta t}{4\mu}\frac{\partial^2}{\partial z^2}\right)\psi(t,\rho,z). \tag{8}$$

The item with the second derivative to z can be performed directly with the method of fast Fourier transform (FFT) [24], and in order to calculate the other item relative to ρ, some approximations should be made

$$\left[1 - \left(\frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho}\frac{\partial}{\partial\rho}\right)\frac{i\hbar\,\delta t}{4\mu}\right]\psi(t+\Delta t,\rho,z)$$
$$= \left[1 + \left(\frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho}\frac{\partial}{\partial\rho}\right)\frac{i\hbar\,\delta t}{4\mu}\right]\psi(t,\rho,z), \tag{9}$$

$$-\frac{i\hbar}{2\mu}\left(\frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho}\frac{\partial}{\partial\rho}\right)\psi_\rho^{t+\Delta t}$$
$$= -\frac{i\hbar}{2\mu}\left(\frac{\psi_{\rho+\Delta\rho}^{t+\Delta t} - 2\psi_\rho^{t+\Delta t} + \psi_{\rho-\Delta\rho}^{t+\Delta t}}{\delta\rho^2} + \frac{1}{\rho}\frac{\psi_{\rho+\Delta\rho}^{t+\Delta t} - \psi_{\rho-\Delta\rho}^{t+\Delta t}}{2\,\delta\rho}\right). \tag{10}$$

Then, we can obtain such a linear equation, which is advanced for $t \to t+\Delta t$

$$-\frac{i\hbar\,\delta t}{4\mu}\left(\frac{1}{\delta\rho^2} + \frac{1}{2\rho\,\delta\rho}\right)\psi_{\rho+\Delta\rho}^{t+\Delta t} + \left(1 + \frac{i\hbar\,\delta t}{2\mu\,\delta\rho^2}\right)\psi_\rho^{t+\Delta t}$$
$$-\frac{i\hbar\,\delta t}{4\mu}\left(\frac{1}{\delta\rho^2} - \frac{1}{2\rho\,\delta\rho}\right)\psi_{\rho-\Delta\rho}^{t+\Delta t}$$
$$= \frac{i\hbar\,\delta t}{4\mu}\left(\frac{1}{\delta\rho^2} + \frac{1}{2\rho\,\delta\rho}\right)\psi_{\rho+\Delta\rho}^{t} + \left(1 - \frac{i\hbar\,\delta t}{2\mu\,\delta\rho^2}\right)\psi_\rho^{t}$$
$$+ \frac{i\hbar\,\delta t}{4\mu}\left(\frac{1}{\delta\rho^2} - \frac{1}{2\rho\,\delta\rho}\right)\psi_{\rho-\Delta\rho}^{t}. \tag{11}$$

The boundary condition is chosen the same as those of Corkum *et al.*'s work [24] to avoid having grid points on the $\rho=0$ singularity. As is known, H_1 and H_2 can be diagonalized in momentum and coordinate space, respectively. The wave function is transformed into momentum or coordinate space during the process of our calculation. Finally, the solution of Eq. (6) is projected to axis Z that is perpendicular to the molecular axis by using the Bessel functions [24]. Solving the Schrödinger equation in three dimensions will increase the accuracy of the energy spectra for both the electrons and the nuclei [23].

The kinetic energy distribution of the H^+ ion can be calculated through a series of transformations based on Eq. (6). The parameters for laser-induced electronic process have been considered to determine the grid space required for calculation [29–31]. During the calculation, $\Delta t = 20$ attoseconds are found to be suitable for the converged results. The parameters, e.g., full width half maximum, laser intensity, wavelengths of the laser pulses used in our calculations are the same as those of Niikura *et al.*'s work [14].

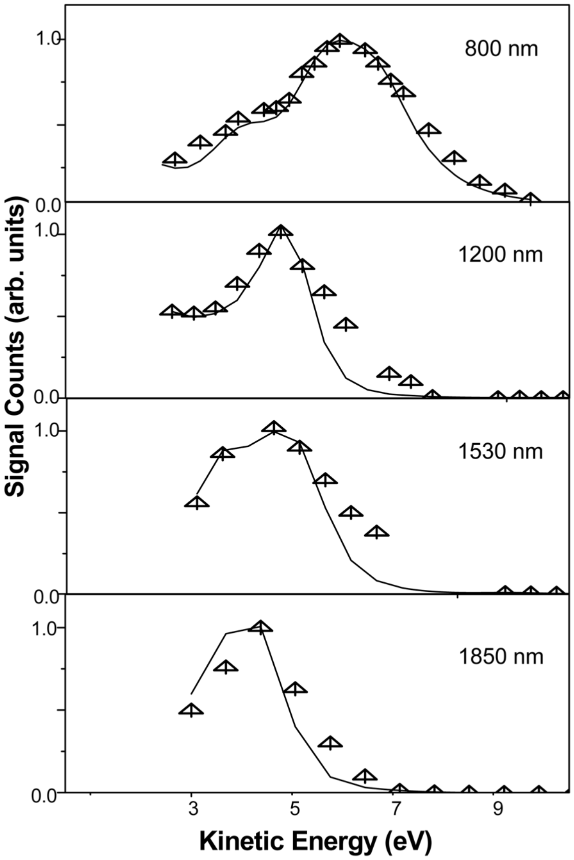

FIG. 2. The comparisons of H^+ kinetic energy distributions between calculated results and experimental obtained (calculated results: solid line; experimental ones: hollow triangles).

III. RESULTS AND DISCUSSION

Figure 2 shows the calculated kinetic energy spectra of H^+ with 800 nm, 1200 nm, 1530 nm, and 1850 nm wavelengths, respectively. Clearly, our calculated results are in agreement with the experimental ones for the different wavelengths [14]. The H^+ ions might be produced from two processes, i.e., recollision of electron with H_2^+ and the further ionization of H_2^+ by laser. With our theoretical model the calculated H^+ ions yields are mainly resulted from recollision between the return electron and its parent ion $H_2^+(X^2\Sigma_g^+)$ for all the wavelengths, which supports the conclusion of Niikura *et al.*'s work [14]. In addition, the active electron will be pulled back several times during the laser pulse, and the contributions of the first and third return are larger than those of any others. The two peaks observed at about 3.5 eV and 5.5 eV in the kinetic energy distribution (at 800 nm) are resulted from the third and first electron return, respectively.

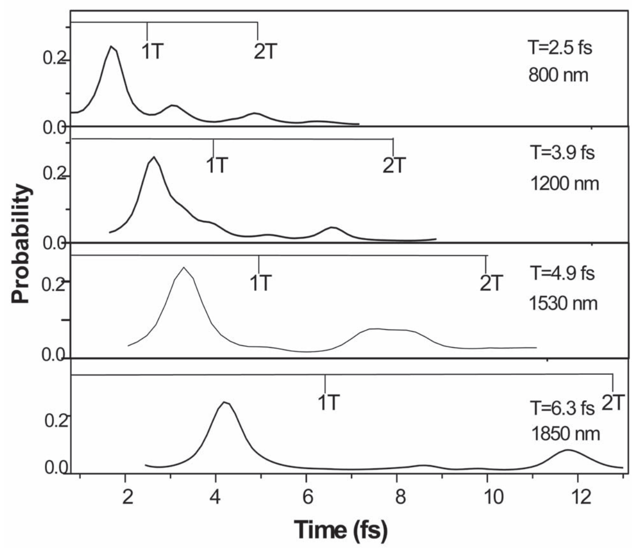

FIG. 3. The probabilities of recollision between electron and its parent ion $H_2^+(X^2\Sigma_g^+)$ with different wavelengths are shown to change with the recollision time.

Because the time-dependent Schrödinger equation of electron coupled with the nuclei is used to solve the entanglement between the ionization electron and H_2^+ ion, the probabilities of the ionic electron returning to recollide with its parent ion can be easily calculated. In addition, the electronic wave function becomes stationary on 0.9 fs during a field-induced transition [19], and the relaxation time is with 10 as time scale for H_2 [26]. So the electron will return several times to recollide with its parent ion during 40 fs laser pulse, and each recollision time can also be calculated with our model.

The recollision probabilities are shown as a function of time in Fig. 3. It is obviously found that the distribution of the probabilities strongly depends on the wavelengths, and the electron returns to its parent ion several times in two optical periods, but the first return of the electron wave packet dominates. Thus, the highest yield of H^+ ions to each wavelength in Fig. 2 is due to the first electron return to recollide with its parent ion.

In Fig. 4, it is shown that the kinetic energy of H^+ ions are related with the wavelengths, and the peaks at 1.7 fs, 2.6 fs, 3.3 fs, and 4.2 fs are about two thirds of the first optical period according to 800 nm, 1200 nm, 1530 nm, and 1850 nm, respectively. These calculated results accord well with those of the experiment [14], and it is also clearly shown the regularity, i.e., longer wavelength and less kinetic energy.

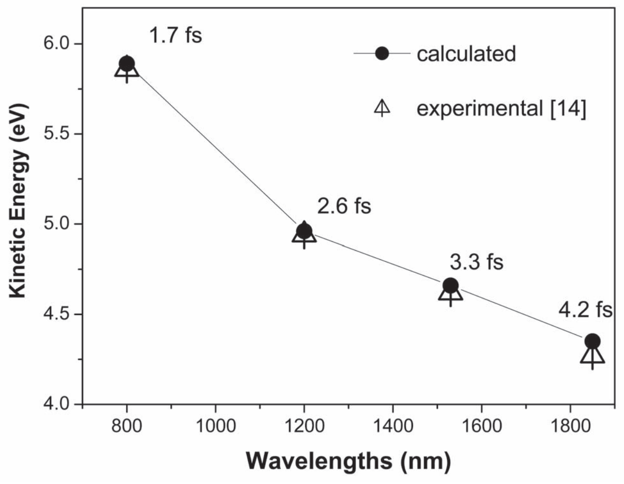

FIG. 4. The relations between the wavelengths and the kinetic energies are shown.

IV. CONCLUSIONS

In summary, the kinetic energy spectra of H^+ ion have been calculated by using the time-dependent-wave-packet method through solving the Schrödinger equation of the electrons coupled with the nuclei. The probabilities of recollision between the electron and its parent ion have also been calculated. We find that the H^+ ions mostly come from the dissociation of H_2^+ by the first electron return in the first optical period, and the definite recollision time is given. In addition, it can be easily found that most recollision events occurred during the first two optical periods in H_2 system. However, there are several recollision events appeared in the third optical period in its isotope D_2 system [16]. For the reason that the recollision is the three-step process responsible for the high-order harmonic generation (HHG) [5], so we also predict that heavier isotopes will generate more intense harmonics [6].

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