Correlation Quantum Dynamics between an Electron and D_2^+ Molecule with Attosecond Resolution

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Recently, Niikura *et al.* [Nature (London) **421**, 826 (2003)] have applied the entanglement approach to exploit the correlation between the electronic and nuclear wave packets. Here, we use the time-dependent–wave-packet method to calculate the kinetic energy distribution of the D^+ ion resulting from the recollision between an electron and its parent ion $D_2^+(X^2\Sigma_g^+)$ within the attoseconds time scale. Our theoretical results of the D^+ ion kinetic energy spectra accord well with the experimental ones, and the recollision probabilities between the electron and the D_2^+ molecule have been calculated.

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The remarkable progress of the femtosecond laser in recent years has attracted the attention of many scientists. A lot of ultrafast molecular dynamics phenomena including coherent control of molecular systems [1] have been extensively investigated [2]. But electron dynamics occurring at an attosecond time scale can only be probed by the attosecond resolution method. Fortunately, single attosecond pulses have appeared with the dedication of great efforts [3–8]. Drescher *et al.* studied the time-resolved electron spectroscopy of atomic inner-shell using attosecond extreme ultraviolet light source [4,9]. Recently, Niikura *et al.* proposed an entanglement method to probe the D_2^+ vibrational wave packet over a few femtoseconds with sub-fs resolution. In Niikura *et al.*'s experiment [10], a 40 fs, 1.5×10^{14} W/cm^2 laser pulse with wavelengths ranging from 800 nm to 1850 nm was used to ionize the D_2 molecule. They predicted that the D^+ ions mainly result from the recollision between the electron and its parent ion, and the attosecond bound-state wave-packet dynamics have been fully characterized in their up to date work by solving the 1D time-dependent Schrödinger equation [11]. In contradiction to this, with a rescattering theoretical model, Tong *et al.* propose that the D^+ ions are produced mainly not from the dissociation of the D_2^+ ion after excited by the returning electron, but rather by the Coulomb explosion after the excited state D_2^+ is further ionized by the laser [12].

It has long been known that the recollision between an electron and its parent ion is responsible for high-harmonics emission [13,14] and correlated multielectron ionization in strong laser fields [15]. The probability of an electron recolliding with the parent ion reaches a maximum at a well-defined laser phase, about two-thirds of an optical period after the electron's transition to continuum [10]. Niikura *et al.* predicted that the return of the electron wave packet in the first optical period dominates [10], but Tong *et al.*'s analysis shows some differences [12]. In order to shed a light on resolving the contradictions, we present a three dimensions (3D) time-dependent–wave-packet method to calculate the motion of the electrons and nuclei, i.e., electron in two dimensions and nuclei in one dimension. The split operator scheme is used to calculate the time-resolved kinetic energy spectra of D^+ and the probability of recollision between the returning electron and its parent ion $D_2^+(X^2\Sigma_g^+)$. In view of the time scale, it takes much longer (about 50 fs) for the nuclei to settle into a stationary state, and the electronic wave function becomes stationary on 0.9 femtosecond during a field-induced transition [16]. So the Schrödinger equation in cylindrical coordinates can be written separately as [17,18]:

$$i\hbar\frac{\partial}{\partial t}\psi_{\mathrm{I}}(\rho, z, \theta, t) = \left[-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho}\frac{\partial}{\partial\rho} + \frac{\partial}{\partial z^2} + \frac{\partial}{\partial\theta^2}\right) + V(R, \rho, z, t)\right]\psi_{\mathrm{I}}(\rho, z, \theta, t), \quad (1)$$

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

Equation (1) depicts the motion of the electrons, and the azimuthal electron coordinate will be eliminated by symmetry in our calculation. The z is along the molecular axis. The laser polarization is not considered during our calculation to the electron for the reason that the electron wave packet spreads spatially both parallel and perpendicular to the laser polarization axis after ionization [19].

In Eq. (1), R is the internuclear distance, (ρ, z, t) is the cylindrical coordinates of the recollision electron, and that of the bound electron is included in the potential of the D_2^+. The item $-\frac{\hbar^2}{2\mu}(\frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho}\frac{\partial}{\partial\rho} + \frac{\partial}{\partial z^2})$ denotes the kinetic energy of the electrons, and $-\frac{\hbar^2}{m_p}\frac{\partial^2}{\partial R^2}$ is the kinetic energy of the nuclei. The item μ is the reduced mass of the electrons. The potential energy $V(R, \rho, z, t)$ includes several parts: $V(R, t)$, V_R, 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 ($\hbar$, m_e, α, and c denote the Planck constant, one electron mass, fine structure constant,

and the speed of light, respectively). The item $V(R, t)$ is the potential energy of the bound electron in the strong laser field, and $V_R = \frac{e^2}{R}$ can be neglected in our calculation. Meanwhile, the item V_C is the Coulomb interaction between the recollision electron and the nuclei, where

$$V_C = -\frac{1}{\sqrt{\rho^2 + (z - R/2)^2}} - \frac{1}{\sqrt{\rho^2 + (z + R/2)^2}}. \quad (3)$$

Because there is only one bound electron as to the D_2^+ molecule, it is not necessary to consider the correlated interaction of the electrons, except that the recollision electron is pulled back by the laser field to recollide with its parent ion. However, in hydrogenlike atoms due to the frictional force the electron moves with the constant velocity $V = \alpha c$, and it only can be observed by the very short laser pulses, such as those of attoseconds [20]. So we introduce an additional item $-2\Gamma\hbar\frac{\partial^2}{\partial t^2}$ to denote the correlated interaction between the bound electron and the recollision one, and this additional item was introduced by Kozlowski and Marciak-Kozlowska as a kind of frictional force to describe the interaction of the electron with its surrounding in atom [20]. So we believe it is worthwhile to apply this additional item to describe the interaction of the two electrons during the very short laser pulses. The potential energy $V(R, \rho, z, t)$ can be written similarly to the form of our previous works [21,22], but the coulomb interaction V_C and the correlated interaction $V_\Gamma = -2\Gamma\hbar\frac{\partial^2}{\partial t^2}$ are added to each diagonal and off-diagonal item of the discretized set of continuum states $A^2\Sigma_u^+$.

The wave function of the electrons is calculated by Eq. (1) in order to solve the correlated problem in such short laser pulses, and both these two electrons have the probability to be ionized because the D_2^{++} state is included in the ionic state of the bound electron. The initial wave function in Eq. (1) denoting the ground state of D_2 can be written as

$$\Psi_{\text{in}}(\rho, z, 0) = \psi(\rho, z, 0)\psi(\rho, 0) = \psi(\rho, z, 0)\rho e^{\frac{-\Delta t\rho}{2\Gamma}}. \quad (4)$$

Where $\Psi_{\text{in}}(\rho, z, 0)$ with the type of Slater [23] denotes the motion of the recollision electron and the bound electron, respectively.

The ''split-operator Fourier'' method [21,22] is used to solve this time-dependent Schrödinger equation (1).

$$\psi(t + \delta t, \rho, z) = \exp\left(-\frac{iH_1}{2\hbar}\delta t\right)\exp\left(-\frac{iH_2}{\hbar}\delta t\right) \times \exp\left(-\frac{iH_1}{2\hbar}\delta t\right)\psi(t, \rho, z) + O(\delta t^3) \quad (5)$$

where

$$H_1 = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho}\frac{\partial}{\partial\rho} + \frac{\partial^2}{\partial z^2}\right), \qquad H_2 = V_c + V(R, t) - 2\Gamma\hbar\frac{\partial^2}{\partial t^2}. \quad (6)$$

Finally, the solution of Eq. (5) is projected to axis z that is perpendicular to the molecular axis by using the Bessel functions [24]. Solving the Schrödinger equation in 3 dimensions will increase the accuracy of the energy spectra for both the electrons and the nuclei [25].

During the calculation, $\Delta t = 20$ as is found to be suitable for the converged results. The parameters, e.g., full-width-half-maximum, laser intensity, wavelengths of laser pulses, used in our calculations are the same as those in the experiment [10].

Figure 1 shows the calculated kinetic energy spectra of D^+ with 800, 1200, 1530, and 1850 nm wavelengths, respectively. Clearly the calculated results are in excellent agreement with the experimental ones for all the wavelengths [10]. Except the instance of 800 nm, the double ionizations (D_2^{++}) can be seen in the cases of other three wavelengths. This is also in agreement with experimental observation. These results show the present theoretical method could correctly describe the experimental phenomena observed by Niikura *et al.* [10].

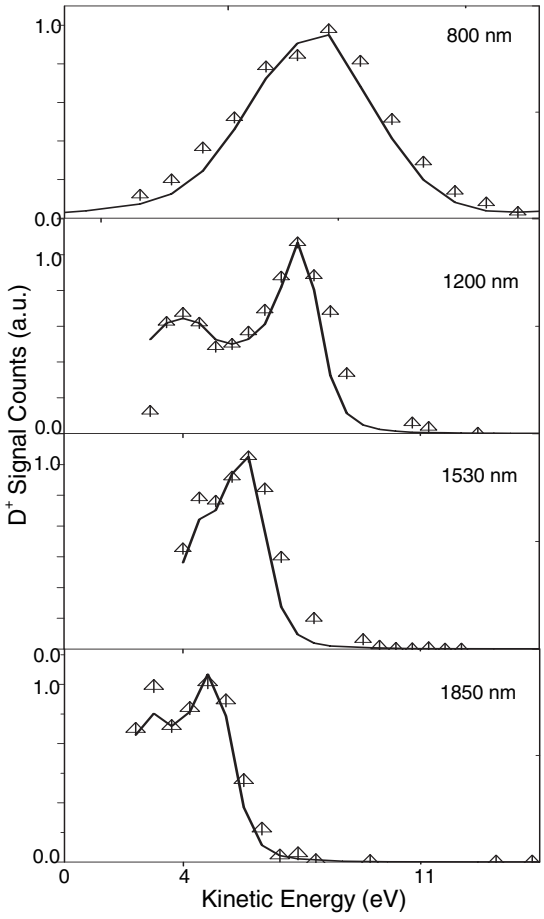

FIG. 1. The comparisons of D^+ kinetic energy distributions between calculated results and experimental obtained (simulated result, solid line; experimental obtained, hollow triangles).

The D^+ ion might be produced from two processes, i.e., recollision of electron with D_2^+ and the further ionization of D_2^+ by laser. Niikura *et al.* predicted that the production of the D^+ ion was dominated by recollision [10], while Tong *et al.* concluded that the main peak was due to the further ionization of the excited D_2^+ by the laser [12]. The calculated D^+ kinetic energy spectra resulted from the electron recollision and the laser further ionization are presented in Fig. 2. It can be easily seen that over 80% of D^+ ions result from the recollision between the electron and its parent D_2^+ ion for all the wavelengths. Therefore, we conclude that the recollision process is dominant for the yields of D^+ ions.

Because of that we solve the time-dependent Schrödinger equation of electron coupled with the nuclei; the entanglement between the ionization electron and $D_2^+(X^2\Sigma_g^+)$ ion is automatically included. Therefore, we can depict the physical picture on the entanglement, and the recollision probability of the electron returning to the parent ion is easily calculated. Figure 3 shows the position of the vibrational wave packet when the largest recollision probability occurred. Obviously the distributions of the recollision probabilities strongly depend on the wavelengths. Moreover, our calculations show that the electron returns to its parent ion several times but the first return of the electron wave packet dominates, which is in agreement with the prediction of Niikura *et al.*'s work [19]. Figure 4 shows the recollision probability as a function of time. The peaks at 1.7 fs, 2.6 fs, 3.3 fs, and 4.2 fs, which appear at two-thirds of the first optical period, are contributions of the first electron return at 800, 1200, 1530, and 1850 nm, respectively. The durations of the first electron return range from 1 to 2 fs. The recollision probabilities in other optical periods are quite low and thus the contributions from the second circle are negligible. Our calculations strongly support Niikura *et al.*'s ideas, e.g., an electron wave packet produced during intense fields could be used for probing molecular dynamics with an attosecond resolution and the time delay between the creation of the correlated wave packets and their recollision is controlled by changing the laser wavelength [10].

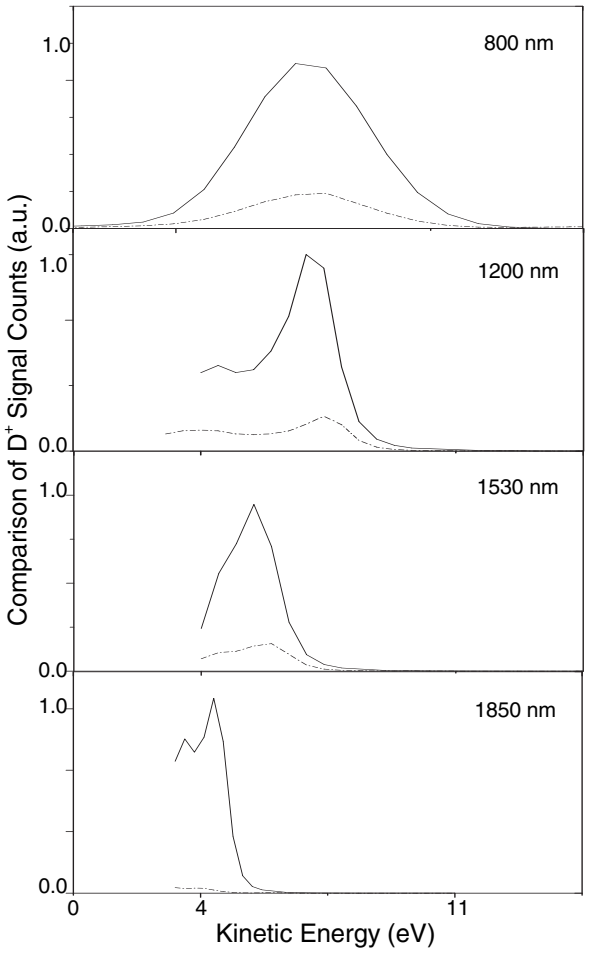

FIG. 2. Two different D^+ yields resulting from the recollision and further ionization (recollision yields, solid lines; further ionization, dashed-dotted lines).

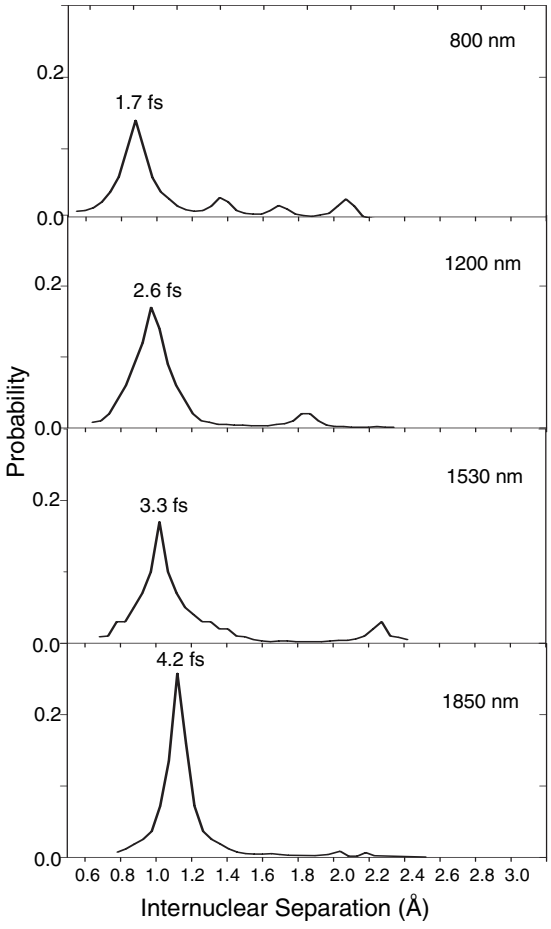

FIG. 3. The probabilities of recollision between an electron and its parent ion $D_2^+(X^2\Sigma_g^+)$ with different wavelengths are shown.

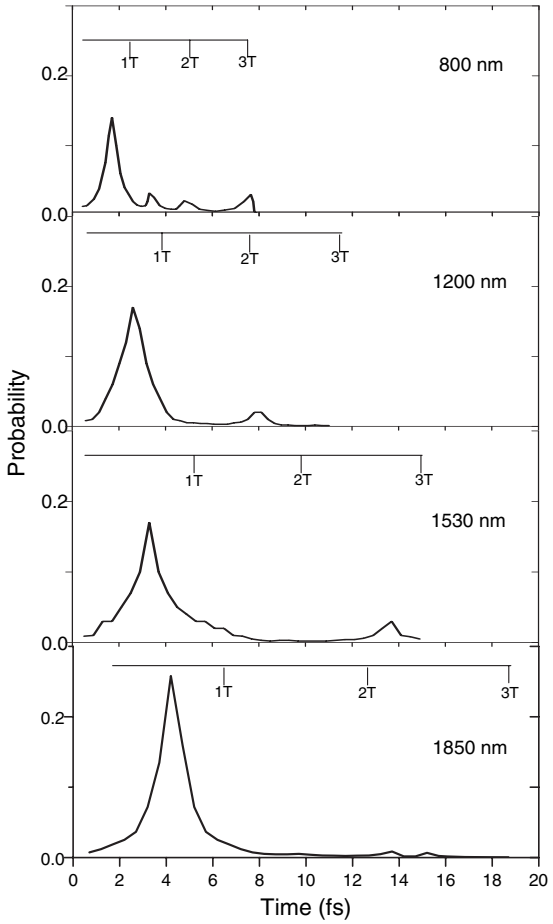

FIG. 4. The probabilities of recollision between an electron and its parent ion $D_2^+(X^2\Sigma_g^+)$ with different wavelengths are shown to change with the recollision time.

In summary, the kinetic energy spectra of D^+ ion from the experiment [10] have been well reproduced 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 been calculated. We find that the D^+ ions mostly come from the dissociation of D_2^+ by the first electron return in the first optical period. Also, we agree with Niikura *et al.* that the kinetic energy distribution of D^+ ion spectra from the intense field can be used for probing molecular dynamics with attosecond resolution.

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