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Time-resolved sequential double ionization of D_2 molecules in an intense few-cycle laser pulse

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The kinetic energy spectra of D^+ ions resulting from the sequential double ionization of D_2 molecules in an intense few-cycle laser field are calculated. The D_2 molecule is first ionized at its equilibrium distance, followed by further ionization of D_2^+ at larger internuclear separations. The time evolution of the nuclear wave packet is calculated including loss from ionization by the time-dependent laser field. The calculated D^+ energy spectra are compared with the recent experiment, and the time duration between the two ionization events is deduced to subfemtosecond accuracy.

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I. INTRODUCTION

In a recent paper, Legare *et al.* [1] reported experiments on the double ionization of D_2 molecules by an intense few-cycle laser pulse. For a laser pulse of duration of 8–10 fs and peak intensity of about 10^{15} W/cm^2, they measured the kinetic energy spectra of the D^+ ions, from which they deduced the time interval between the two ionization events. For example, for a linearly polarized laser of 8.6 fs duration and peak intensity of 2.8×10^{15} W/cm^2, the authors deduced that the second ionization is complete within about 4 fs after the occurrence of the first ionization. By using simple models for the ionization rates for molecules [2], their calculated kinetic energy release spectra of D^+ ions differ to some extent from the experimental data. As noted by the authors [1], sequential double ionization of D_2 by an intense few-cycle laser pulse can serve as a molecular clock. This is to be compared to the earlier works on D_2 molecules by lasers of longer pulses (about 25–40 fs) and lower peak intensity (about 1.5×10^{14} W/cm^2) [3–7]. In the latter rescattering by the returning ionized electron was found to be the main mechanism for the dissociation and ionization. From the released kinetic energy spectra of the D^+ ions both types of experiments can be used to measure the time of double ionization of D_2 at subfemtosecond accuracy. To provide a firmer interpretation of such experiments in the higher intensity region by few-cycle pulses where ionization by rescattering is not important, we carried out this theoretical study to obtain the kinetic energy spectra of D^+ ions resulting from the sequential double ionization. Accurate static ionization rates at each internuclear separation are used and the loss of the vibrational wave packet due to the laser ionization is also accounted for. From the rate equation for the probability of the second ionization we calculated the kinetic energy spectra to compare with the data of Legare *et al.* We also studied the dependence of the kinetic energy spectra with respect to the pulse length, showing that the time interval between the two ionizations depends critically on the pulse length. We will introduce our theoretical method in Sec. II and present our results and comparison with the experiment in Sec. III, followed by a conclusion in Sec. IV.

II. THEORETIC METHOD

Since the first ionization occurs around the equilibrium distance of D_2, the rate for the first ionization can be described by the molecular tunneling ionization model introduced recently [8]. The validity of this model as a function of the internuclear separation will be discussed in detail later. The first ionization probability of D_2 at time t_1 can be written as (atomic units, $m=\hbar=e=1$, are used throughout the paper unless otherwise indicated)

$$dP_1(t_1) = W_1(t_1)e^{-\int_{-\infty}^{t_1} W_1(t')dt'}dt_1, \tag{1}$$

where W_1 is the first ionization rate.

The probability of the second ionization to occur at time t and internuclear separation R for which the first ionization occurs at t_1 is

$$d^2P_2(R,t_1,t) = W_2(R,t)\chi^2(R,t-t_1)dtdR, \tag{2}$$

where $\chi(R,t-t_1)$ is the time-dependent wave function describing the vibrational wave packet created at time t_1. It is obtained by solving the time-dependent Schrödinger equation

$$i\frac{\partial}{\partial t}\chi(R,t) = H_g\chi(R,t) - i\frac{W_2(R,t)}{2}\chi(R,t), \tag{3}$$

using the pseudospectral grid method in the energy representation [9]. In this equation, H_g is the Hamiltonian for the vibrational motion in the ground potential curve of D_2^+ and $W_2(R,t)$ is the static field ionization rate of D_2^+ calculated for internuclear separation R and laser electric field at time t. The equation is to be solved with the initial condition $\chi(R,0)=\chi_g(R)$, the ground vibrational state of D_2, in the ground electronic state. The probability density for sequential double ionization to occur at internuclear separation R is then given by

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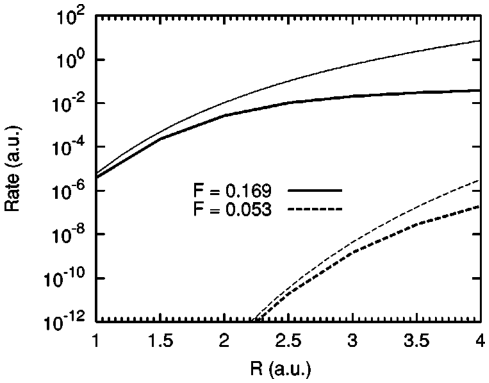

FIG. 1. Static ionization rates of D_2^+ as a function of internuclear separation at two field strengths. The thick lines are from the complex-scaling calculations and the thin lines are from the MO-ADK model. The electric field is parallel to the molecular axis.

$$\begin{aligned}\frac{dP(R)}{dR} &= \int\int dP_1(t_1)dP_2(R,t_1,t)\\ &= \int_{-\infty}^{\infty}\int_{t_1}^{\infty} W_1(t_1)e^{-\int_{-\infty}^{t_1}W_1(t'')dt''}W_2(R,t)\chi^2(R,t-t_1)dt_1dt\\ &= \int_0^{\infty}\frac{d^2P(R,\tau)}{dRd\tau}\,d\tau, \qquad (4)\end{aligned}$$

where

$$\frac{d^2P(R,\tau)}{dRd\tau} = \int_{-\infty}^{\infty} W_1(t_1)e^{-\int_{-\infty}^{t_1}W_1(t'')dt''}W_2(R,t_1+\tau)\chi^2(R,\tau)dt_1, \qquad (5)$$

with $\tau = t - t_1$ being the time duration between the two ionizations. This gives the differential double ionization probability where the two ionization events are separated by a time interval τ and the second ionization occurs at internuclear separation R. The second ionization at R would lead to Coulomb explosion and release two ions with a total kinetic energy $E = 1/R$. The total kinetic energy spectra of the D^+ ion pair is then given by

$$\frac{dP}{dE} = R^2\frac{dP}{dR}. \qquad (6)$$

Note that $d^2P(R,\tau)/(dRd\tau)$ contains information about the internuclear separation and the time interval between the two ionizations.

In the equations above, a key input parameter is the static ionization rate $W_2(t)$, which is a function of the internuclear separation and the instantaneous laser field strength at time t. We used the accurate static ionization rates obtained from the complex-scaling method for the two-center D_2^+ system [10]. Figure 1 compares the static ionization rates calculated from the molecular tunneling ionization model (MO-ADK) [8] with those from the complex-scaling method at two field strengths where the field is parallel to the molecular axis. Here we see that the MO-ADK model works at small internuclear separation since the model employs a one-center expansion for the valence electron orbital and it is based on a perturbative approximation. For larger internuclear separation where the second ionization occurs, the MO-ADK rates severely overestimate the ionization rates. Therefore the MO-ADK rate is used only for the first ionization. The accurate static rate for the second ionization is obtained from solving the Schrödinger equation directly as discussed above.

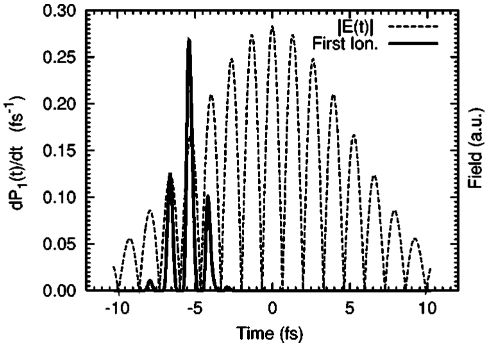

FIG. 2. The time profile of the field strength of a laser pulse of peak intensity 2.8×10^{15} W/cm^2 and pulse length 8.6 fs, with center wavelength at 800 nm. The single ionization probability of D_2 in this laser field as a function of time is also displayed.

III. RESULTS AND DISCUSSIONS

Now let us apply this theoretical method to study the sequential double ionization of D_2 by both linearly and circularly polarized laser pulses. Since the ionization rates for D_2 and D_2^+ are almost isotropic [1,8] we do not consider the alignment effects here.

A. Linearly polarized laser pulses

First we consider double ionization by a linearly polarized laser pulse with a peak intensity of 2.8×10^{15} W/cm^2 and a duration of 8.6 fs as employed in the experiment of Legare *et al.* The time dependence of the magnitude of the laser field strength is depicted in Fig. 2. From Fig. 2 it is clear that more than half of the D_2 molecules are ionized within half of an optical cycle, with the remaining ionization occurring within half of an optical cycle on either side of this peak. The first ionization of D_2 at t_1 launches a vibrational wave packet which propagates in the ground electronic potential curve of the D_2^+ ion.

In Fig. 3 we show the calculated D^+ energy spectra for the laser pulse depicted in Fig. 2, and the comparison with the experimental spectra reported by Legare *et al.* We note that there is a general good agreement between the theory and experiment (the experimental spectra are normalized to the theory at the peak). The peak occurs at about 6.5 eV per ion from which we can deduce that the second ionization occurs at internuclear separation of about 2.2 a.u. In this figure we also demonstrated how the peak position of the ion spectra shifts slightly to the lower energy region if the peak intensity is decreased.

Although the simulated results are in reasonable agreement with experiment, we wish to draw information about the time duration between the two ionizations. For a more

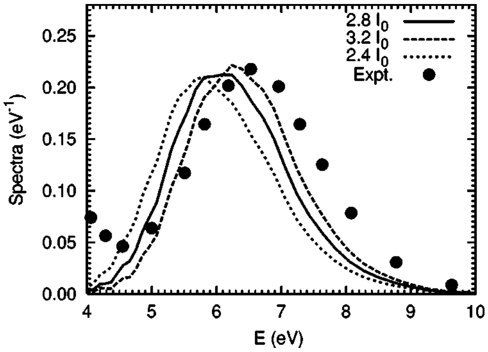

FIG. 3. D^+ pair energy spectra due to the sequential double ionization obtained from the present calculation at three intensities. The experimental data are from Ref. [1] with a peak intensity of 2.8 I_0 where $I_0 = 10^{15}$ W/cm^2. The pulse duration is 8.6 fs.

complete picture of sequential double ionization we show the time dependence of the second ionization at different internuclear separations after the first ionization. In Fig. 4 we display $d^2P(R,\tau)/(dRd\tau)$, the probability density of second ionization occurring at τ and at internuclear separation R. Clearly the second ionization occurs mostly around $\tau = 4$ fs which is about three half optical cycles later after the first ionization, and at internuclear separations of about 2.2 a.u. (first ionization occurs at 1.4 a.u.). The sharpness of the distribution indicates that the time can be read with subfemtosecond accuracy and the internuclear distance can be read with the accuracy of a fraction of an angstrom.

B. Dependence on pulse durations

The analysis of Fig. 4 indicates that the time interval between two ionization events can be varied by changing the pulse length of the laser. To illustrate this, we show in Fig. 5 the probability density distribution of the second ionization for two other pulses with pulse lengths of 5 and 12 fs, respectively, at the same peak intensity of 2.8×10^{15} W/cm^2. Clearly we can see that the second ionization occurs at two half optical cycles for the former, and four half optical cycles for the latter, after the first ionization. Together with the result for the 8.6 fs pulse where the second ionization occurs at three half optical cycles after the first ionization, the sequential double ionization of D_2 offers a means to measure clocks at the discrete steps of half optical cycles, or in periods of 1.3 fs if the laser mean wavelength is 800 nm. These times can be read to subfemtosecond accuracy due to the sharpness of the peaks, or to the strong dependence of the tunneling ionization rates on the electric field strength.

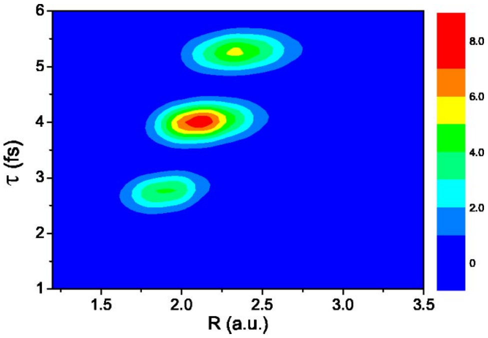

FIG. 4. (Color online) Second ionization probability of D_2^+ as a function of internuclear separation and the time following the first ionization. The laser pulse is linearly polarized, with peak intensity 2.8×10^{15} W/cm^2 and pulse length 8.6 fs.

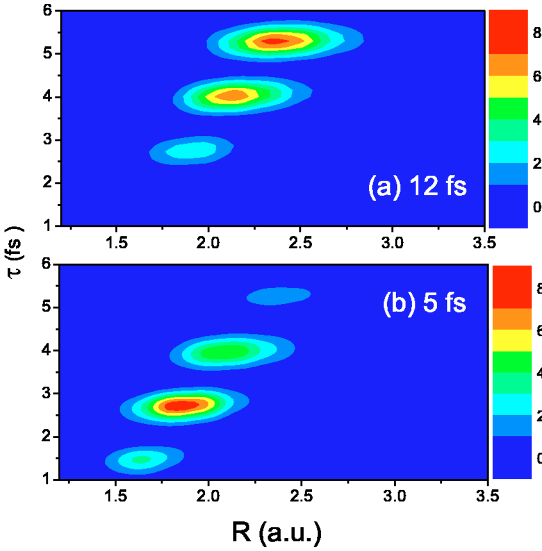

FIG. 5. (Color online) Second ionization probability distribution of D_2^+ vs time and R following the first ionization of D_2. The lasers are linearly polarized, with peak intensities of 2.8×10^{15} W/cm^2 and pulse durations of 5 and 12 fs, respectively.

C. Circularly polarized laser pulses

In the experiment of Legare *et al.* [1], circularly polarized lights with intensities of 1.2×10^{15} and 2.8×10^{15} W/cm^2 and duration of 10.5 fs were also used to doubly ionize D_2 molecules. With such pulses, we show in Fig. 6 the calculated first ionization probability vs time for the two intensities. Clearly the lower intensity pulse has a broader distribution. Different from the linearly polarized light, for circularly polarized light the first ionization probability has no oscillations repeating at half cycles. The calculated D^+ energy spectra are shown in Fig. 7 and compared to the data reported by Legare *et al.* While both theory and experiment show that the

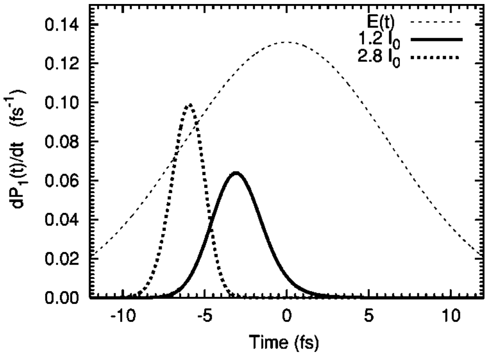

FIG. 6. First ionization probability of D_2 by circularly polarized laser pulses. The peak intensities are 1.2 and 2.8 I_0, respectively, where $I_0 = 10^{15}$ Wcm^2. The pulse length is 10.5 fs.

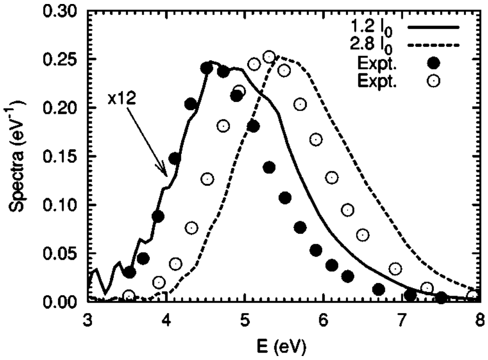

FIG. 7. D$^+$ energy spectra due to the sequential double ionization of D_2 by a circularly polarized laser pulse. The experimental data are from Ref. [1]. The peak intensity of the circulary polarized laser are 1.2 and 2.8 I_0 where $I_0 = 10^{15}$ W/cm^2. The pulse length is 10.5 fs.

peak position shifts to the higher kinetic energy side as the laser intensity is increased, the D$^+$ kinetic energy spectra predicted by the theory is higher than the experimentally measured ones. Similar to the linear case, we show $d^2P(R,\tau)/(dRd\tau)$ in Fig. 8. Clearly the time and distance where the second ionization occurs are less precisely defined. In other words, sequential double ionization by circularly polarized light does not make as good a molecular clock in that the time and distance of the second ionization spread over a broader range. The simulation shown in Fig. 7 indicates that the D$^+$ ion spectra depend sensitively on the peak laser intensity. Since a thin molecular beam was used to eliminate the volume effect in the experiment, the calculation did not account for any possible effect from integration over the volume of the laser pulse. We note that the volume effect is less severe for the linearly polarized pulse since the second ionization occurs only near the peak of each half optical cycle and thus only the electric field near the center can contribute to the second ionization. Furthermore, an error of 20% or so in the calibration of peak laser intensity possibly can also account for most of the discrepancy.

IV. SUMMARY AND CONCLUSION

In this paper we address the mechanism of sequential double ionization of D_2 molecules in a short intense laser pulse. Using accurate tunneling ionization rates for D_2 and D_2^+ and following the time evolution of the vibrational wave packet, we calculated the expected kinetic energy spectra of the D$^+$ ions. The calculated ion spectra are compared to the spectra reported in the experiment by Legare *et al.* [1]. From the simulation, we can draw the conclusion that double ionization occurs sequentially and that the two ionizations occur within 4 fs of each other for a linearly polarized laser pulse of duration of 8.6 fs and peak intensity of 2.8 $\times 10^{15}$ W/cm^2. The simulation also shows that the second ionization occurs at an internuclear separation of 2.2 a.u. We further showed that by changing the duration of the laser pulse, we can change the time interval between the two ionizations, in multiples of half optical cycles. Thus the sequential double ionization of D_2 or H_2 can be used as molecular clocks where the clocks can be read with subfemtosecond accuracy, as proposed by Legare *et al.* Our simulation provides quantitative confirmation of their idea. We also demonstrated that sequential double ionizations by circularly polarized light are not as effective in precisely defining the clock since both first and second ionizations occur over a broader range of time and internuclear distance.

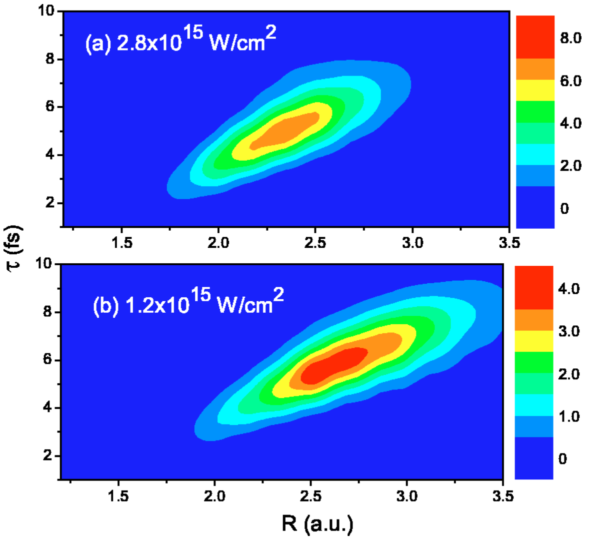

FIG. 8. (Color online) Second ionization probability distribution of D_2^+ vs time and R following the first ionization of D_2. The lasers are circularly polarized, with peak intensities of 2.8×10^{15} and 1.2×10^{15} W/cm^2, respectively, and the pulse length is 10.5 fs.

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[1] F. Legare *et al.*, Phys. Rev. Lett. **91**, 093002 (2003).
[2] G. L. Yudin and M. Y. Ivanov, Phys. Rev. A **64**, 013409 (2001).
[3] H. Niikura *et al.*, Nature (London) **417**, 917 (2002).
[4] H. Niikura *et al.*, Nature (London) **421**, 826 (2003).
[5] A. S. Alnaser *et al.*, Phys. Rev. Lett. **91**, 163002 (2003).
[6] X. M. Tong, Z. X. Zhao, and C. D. Lin, Phys. Rev. A **68**, 043412 (2003).
[7] X. M. Tong, Z. X. Zhao, and C. D. Lin, Phys. Rev. Lett. **91**, 233203 (2003).
[8] X. M. Tong, Z. X. Zhao, and C. D. Lin, Phys. Rev. A **66**, 033402 (2002).
[9] X. M. Tong and S. I. Chu, Chem. Phys. **217**, 119 (1997).
[10] X. Chu and S. I. Chu, Phys. Rev. A **63**, 013414 (2001).