Attosecond xuv pulses for complete mapping of the time-dependent wave packets of D_2^+

X. M. Tong* and C. D. Lin

J. R. Macdonald Laboratory, Physics Department, Kansas State University, Manhattan, Kansas 66506-2604, USA
(Received 31 August 2005; published 21 April 2006)

We have shown that the whole time-dependent vibrational wave packet of D_2^+ ions can be reconstructed from the kinetic energy release of the D^+ ion pairs when it is probed with an attosecond xuv pulse. Such a full interrogation of the wave packet will pave the way for controlling the generation of tailor-designed wave packets for favorable chemical reaction paths, as well as for probing the time evolution of their interaction with the medium.

One of the central problems in modern chemistry is the development of methods for controlling the outcome of a chemical reaction [1]. With the advent of short-pulse lasers, it has been demonstrated in the last decade that the coherent properties of the lasers can be used to manipulate the motion of electrons and nuclei, thus creating favorable pathways where specific reactions can be enhanced. As an example, by using a pair of 70–110 fs laser pulses in a pump-probe experiment on Na_2, it has been observed that the production ratio of Na_2^+/Na^+ undergoes enhancement for certain time delays between the pulses [2]. The enhancement was traced to the motion of the wave packet near the turning points, thus pointing out that knowledge of the time evolution of the complete wave packet is essential to the control of chemical reactions.

Various pump-probe techniques have been suggested and used to deduce the time-dependent wave packets, including tomographic reconstruction from the time-dependent fluorescence spectra [3], and time-resolved photoelectron spectra [4,5]. For dissociating molecules, another direct method is to map out the time-dependent kinetic energy release (KER) of the ions following Coulomb explosion after the probe pulse [6]. For the wave packets of the simplest H_2^+ and D_2^+ molecules, laser pulses of durations of about 80 fs [7], 50 fs [8], and more recently, of 25 fs [9], have been used in pump-probe experiments. Since the vibrational periods of these two molecules are about 15 and 22 fs, respectively, many interesting features of the time-dependent wave packets disappear when they are probed with such long pulses. Glimpse of the wave packet evolution does appear in the recent experiment of Alnaser *et al.* [10] where they used two 8 fs pulses to double ionize H_2 or D_2. By measuring the KER of the fragmented ions vs time delay, "movies" showing the motion of the wave packets on the two lowest potential surfaces have been constructed. While experimental results were found to be in general agreement with the theoretical simulation, many interesting features predicted in the theoretical simulation were not observed experimentally. In the theoretical simulation it was assumed that the initial wave packet was created according to the Franck-Condon (FC) principle (used in almost all models), while in fact, testing the validity of

this assumption should be one of the goals of the experiment. For H_2 and D_2, a recent experiment [11] has shown that the vibrational distributions created by a laser pulse do not follow the FC prediction. While the non-FC distributions have been interpreted in terms of the volume effect in a recent theory [12], it is interesting to ask if there is a direct experimental method to determine not just the vibrational distributions, but the vibrational wave packet itself. Such measurements also would offer a direct look on how the creation of the initial wave packet depends on the shaped pulses, thus gaining a full coherent control in future pump-probe experiments. In this paper we illustrate that the emerging attosecond xuv pulses, with its "white" light and its short durations, would allow the reconstruction of the whole 'movie' of the vibrational wave packet, thus offering opportunities of full control of reaction pathways in chemical reactions.

xuv attosecond pulses with a mean energy of about 95 eV and durations of fractions of 1 fs have been generated recently [13,14]. So far such pulses have been used to determine the Auger lifetime in the time domain [15] and to characterize the electric fields of few-cycle ir lasers [16]. Using the polarization gating method, attosecond pulses have also been created at lower photon energies [17]. Attosecond pulses provide unprecedented time resolution such that the wave packet is frozen during the probe even for the lightest H_2^+ and D_2^+ ions. Probing with xuv pulses is desirable so that molecules can be directly ionized from any internuclear separations with the absorption of a single photon. Since a photoionization cross section of H_2^+ varies weakly with the internuclear separation, the ionization yield would almost reflect the distribution of the wave packet directly, thus bypassing direct dependence on theoretical calculations. Note that time-dependent photoelectron spectroscopy cannot be used to map out the wave packet for attosecond pulses due to their large energy bandwidth. However, the KER of the dissociating or ionizing fragments can be used to bypass this limitation [6]. For D_2^+, for example, the internuclear distance R of the wave packet at the time of ionization is directly calculated from the total KER of the two D^+ ions through the relation $E = 1/R$. We comment that this is the special feature of the Coulomb explosion technique used. In general, especially for the photofragmentation of molecules, the final state interaction is significant and the mapping method discussed here would not work (see Ref. [18]). The basic idea for such an experiment is depicted in Fig. 1.
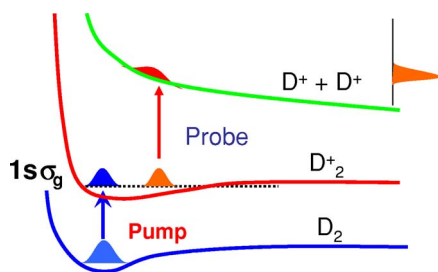
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*Electronic address: xmtong@phys.ksu.edu

FIG. 1. (Color online) Schematic of D_2 double ionization in a pump-probe experiment. The D_2^+ wave packet is created by a pump laser by ionizing D_2. Its subsequent motion is probed via further ionization either by an attosecond xuv pulse or by a sub-10 fs ir laser. The wave packet is to be reconstructed from the KER of the two D^+ ions after the probe pulse.

A short pump pulse is used to create a wave packet by ionizing the D_2 molecule. For simplicity, we assume that D_2^+ is created only in the ground $1s\sigma_g$ electronic state, together with an initial vibrational wave packet. This wave packet will propagate in the $1s\sigma_g$ potential curve. Classically the wave packet is expected to bounce back and forth between the two turning points $R=1.4$ and 4.5 a.u. Quantum mechanically, the motion of this wave packet is much more complicated. For the purpose of simulation, we model that the wave packet was created at $\tau=0$ following the FC principle. With this initial wave packet which is the ground vibrational wave function of the D_2 molecule, the time evolution of this wave packet can be trivially calculated. The top frame of Fig. 2 shows the density plots of its time evolution.

The middle frame shows the result of the simulated wave packet reconstructed from the KER when the wave packet is probed with a 300 attosecond pulse with a mean energy of 50 eV. The bottom frame shows the reconstructed wave packet if it is probed with an 8 fs ir laser pulse, with mean wavelength of 800 nm at an intensity of 9×10^{14} W/cm^2. The latter result is consistent with the observation of Alnaser *et al.* [10] where only a portion of the wave packet is interrogated and the predicted structures have been smoothed out.

To obtain theoretical KER spectra by attosecond pulses, we assume that the intensity is of the order of 10^{12} W/cm^2. In this case ionization can be treated by the first order perturbation theory. For a Gaussian pulse, its intensity profile in the frequency domain is given by

$$I(\omega) \propto e^{-\tau_x^2(\omega - \omega_x)^2/(4 \ln 2)}, \tag{1}$$

where ω_x is the central frequency and τ_x is the attosecond pulse duration. At a given R, the ionization probability is given by

$$P_{ion}(R) \propto \int_{E_b}^{\infty} \sigma(E_b, \omega) I(\omega) d\omega, \tag{2}$$

with E_b the ionization potential of D_2^+ at a given R, and $\sigma(E_b, \omega)$ is the photoionization cross section by a monochromatic photon of frequency ω. Since photoionization cross sections $\sigma(E_b, \omega)$ at a fixed R are not conveniently available
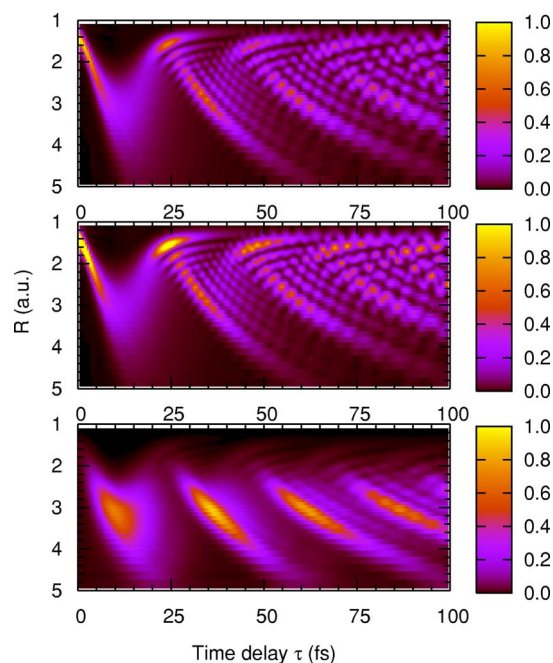

FIG. 2. (Color online)Time evolution of the density distribution of the D_2^+ vibrational wave packet after ionizing D_2 at $\tau=0$, assuming the Franck-Condon principle. (a) "Exact" theoretical wave packet (top frame), (b) reconstructed wave packet from probing with a 0.3 fs xuv pulse with a center energy at 50 eV (middle frame), and (c) reconstructed wave packet from probing with an 8 fs, 800 nm ir laser with an intensity 9×10^{14} W/cm^2 (bottom frame). The middle frame shows that wave packets are reconstructed in verbatim when probed with attosecond xuv pulses.

we chose to use the scaled hydrogenlike photoionization cross sections of atoms [19]

$$\sigma(E_b, \omega) = \frac{2^7}{3Z_s^2} \frac{1}{(1 + \alpha^2)^4} \frac{e^{-4/\alpha \tan^{-1}\alpha}}{1 - e^{-2\pi/\alpha}}, \tag{3}$$

where $\alpha = \sqrt{\omega/E_b - 1}$ and $Z_s = \sqrt{2E_b}$. While more accurate photoionization cross sections can be calculated in the future, we note that the R dependence should be rather reliable with this simple model since the R-dependent ionization potential is included. For $D_2^+(H_2^+)$ the ionization potential is relatively constant except in the small-R region; the photoionization cross sections do not vary much within the range of R of interest. To obtain the ionization rate from a wave packet at time τ after the pump pulse, we calculated

$$\frac{dP(R, \tau)}{dR} \propto |\chi_g(R, \tau)|^2 P_{ion}(R), \tag{4}$$

where $\chi_g(R, \tau)$ is the vibrational wave packet at time τ. After ionization by the probe pulse, the experimentally measured KER spectra per unit energy are obtained from

$$\frac{dP(E, \tau)}{dE} = R^2 \frac{dP(R, \tau)}{dR}. \tag{5}$$

In this calculation the D_2^+ ion is assumed to be stationary during the probe. This is certainly valid for a 0.3 fs pulse.
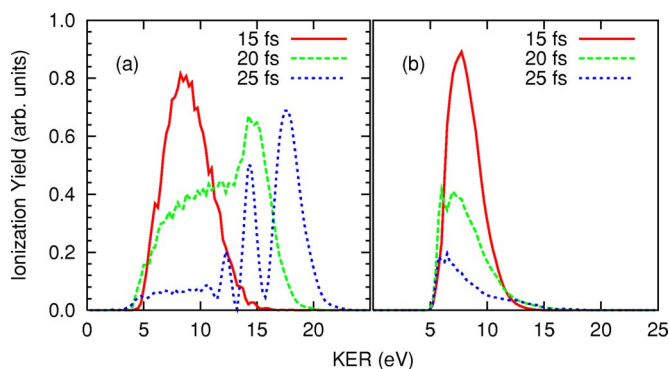
FIG. 3. (Color online)Simulated "experimental" total KER spectra of the two D^+ ions at three time delays, from probing the wave packet of D_2^+ by ionizing with (a) a 300 attosecond xuv pulse and (b) an 8 fs IR laser with intensity at 9×10^{14} W/cm^2.

If the probe pulse is an 8 fs ir laser with intensity of $10^{14}-10^{15}$ W/cm^2, then

$$\frac{dP(R,\tau)}{dR} \propto \int W(R,E(t))|\chi_g(R,t+\tau)|^2 dt. \qquad (6)$$

Here, W is the static tunneling ionization rate of D_2^+ when the internuclear distance is R and the field strength of the probe laser is $E(t)$. For such a "long" pulse, the ionization rate has to be integrated over the pulse duration. The static tunneling ionization rate W has been calculated using the complex rotation method [20]. The tunneling ionization rates depend exponentially on the ionization energy and drop steeply at smaller internuclear distances.

In Figs. 3(a) and 3(b) we show the typical KER spectra calculated when the probe pulse is an attosecond pulse or an 8 fs laser, respectively. This is the expected KER spectra, to be obtained from experiments, if the initial wave packet was created following the FC principle. The spectra were taken at $\tau=15$, 20, and 25 fs after the pump pulse is over. Clearly with attosecond pulses, the KER spectra show many fine structures, and the energy profile shifts with the time delay. In contrast, the KER spectra from the 8 fs laser probe are limited to a fixed energy range of $5-12$ eV. By changing the time delay, only the yield is changed. For such laser pulses, ionization is through tunneling which decreases exponentially with increasing ionization potentials. This results in, as shown in the bottom frame of Fig. 2, that the wave packet is probed only when the internuclear distance is around $3-4$ a.u. In contrast, with an attosecond xuv pulse, the whole range of the wave packet is mapped out, as shown in the middle frame of Fig. 2.

We next examine the time evolution of the calculated and the reconstructed wave packets by attosecond probe pulses in more details. From the top frame of Fig. 2, we note that within the first half vibrational period this wave packet simply propagates outward with gradual broadening. However, upon first reflection from the outer turning point, the wave packet broadens substantially. We show the wave packets for $\tau=15$, 20, and 25 fs in Figs. 4(a) and 4(b).

At first glance indeed the reconstructed wave packet [Fig. 4(b)] reproduces the theoretical wave packet [Fig. 4(a)] in
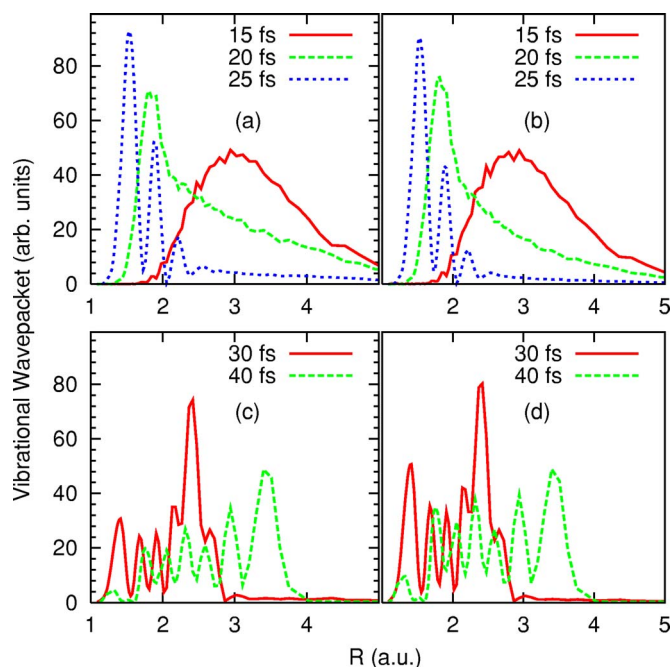

FIG. 4. (Color online)Detailed comparison of the wave packets at different delay times between the theoretically calculated wave packets [(a) and (c)] and those reconstructed [(b) and (d)] from the "measured" KER spectra after ionization of D_2^+ by a 0.3 fs xuv pulse. The time delays are given in each frame.

verbatim at each delay time. At $\tau=15$ fs (recall that the half period is 11 fs), we note that the wave packet spreads almost over a range of about 2.5 a.u. This spreading indeed is surprisingly fast in view that the width of the initial wave packet is only about 0.3 a.u. At $\tau=20$ fs (before reaching the first full period), we begin to see a pileup of the wave packet near the inner classical turning point. This is understood by noting that the frontal part of the wave packet slows down near the turning point earlier so the rear part of the wave packet catches up. After one cycle, say at $\tau=25$ fs, pronounced interference from the incoming and outgoing parts of the wave packet begins to appear. The interference becomes even more complicated at later times, see Figs. 4(c) and 4(d) for $\tau=30$ and 40 fs. We note that there are more interference peaks at these later times and the wave packets are advancing toward larger R, but they are not localized at all. The additional peaks are due to the faster components of the wave packet at smaller R catching up and interfering with the slower components of the wave packet at larger R, similar to the observations made on I_2 molecules with two pump pulses [21].

The result of the present simulation points out the tremendous potential of attosecond pulses in future time-domain experiments. In our simulation, we assumed that the D_2^+ wave packet was created at $\tau=0$ following the FC principle. As pointed out earlier, a recent experiment by Urbain *et al.* [11] showed that this is not true. In fact, by measuring the relative populations of the vibrational levels after the pump pulse, these authors found that the concentration favors the lowest few vibrational levels, and their relative populations change with laser intensity. Since the amplitude of each vi-

brational level is a complex number, measurements of the relative vibrational distributions alone (an energy-domain measurement) do not allow a reconstruction of the initial wave packet. On the other hand, the simulation presented here indicates that the density distribution of the whole wave packet at each time delay can be measured directly with high precision using attosecond pulses. By taking the measurements for different time delays, the complex amplitudes for all the vibrational levels after the pump pulse can be easily recovered (by a linear fitting procedure). This is particularly interesting since it points out that the whole wave packet can be determined in a single experiment at different time delays. Comparing to the so-called coherent and correlation measurements [22] in the energy domain where the number of experiments needed is nearly equal to twice the number of unknown complex amplitudes, this time-domain measurement is by far much simpler. With the robust probing of the vibrational wave packet using attosecond xuv pulses, their coherent control akin to that for rotational wave packets [23] should also be possible.

The ability to readily map out the whole wave packet in the time domain also points out the many roles attosecond pulses will play in chemistry. One can study directly how the initial wave packet depends on the light field of the pump laser, thus paving the way for creating designer's wave packets to follow favorable reaction paths. For example, can one create a wave packet so that it does not spread so quickly as in the present simulation, i.e., closer to a coherent state in a harmonic oscillator? With simple feedback algorithms it may be possible to do so experimentally in real time. Since the attosecond pulses can map out the wave packet so faithfully, other time dependence studies should be possible, including the interaction of the wave packet with its environment, and its loss of coherence with time, especially in a condensed medium.

Are attosecond pulses available today ready for such experiments? Take the ionization cross section for the attosecond pulses at 10^{-19} cm^2, and the density of D_2^+ at 3×10^{12} ions/cm^2 for a path length of 0.3 cm, we calculated the ionization probability to be 10^{-7} per photon. Using the presently available attosecond xuv pulses of $10^7 - 10^9$ photons per pulse, this would yield $1-100$ photoionization events per shot for the KER measurement. To get the quoted density of D_2^+ ions from the pump pulse, one can adjust its intensity together with the density of the D_2 gas. To reduce the noise, double ionization of D_2 by the pump pulse or the probe pulse should be small. However, even if they do occur, their KER spectra are located at the higher energies and they can be subtracted by ionizing D_2 with the pump pulse or the probe pulse separately.

In summary we have shown that attosecond xuv pulses can be used to probe the time evolution of the whole vibrational wave packet created in a pump pulse with unprecedented spatial resolution, in addition to the attosecond time resolution, by measuring the KER of the dissociation or ionization products. The time-dependent KER spectra allow a simple reconstruction of the whole time-dependent wave packet which are invaluable for controlling the generation of tailored-designed wave packets for favorable chemical reactions, or for interrogating the time dependence of its interaction with the environment.

[1] R. J. Gordon and S. A. Rice, Annu. Rev. Phys. Chem. **48**, 601 (1997).

[2] A. Assion, T. Baumert, J. Helbing, V. Seyfried, and G. Gerber, Phys. Rev. A **55**, 1899 (1997).

[3] T. J. Dunn, I. A. Walmsley, and S. Mukamel, Phys. Rev. Lett. **74**, 884 (1995).

[4] A. Assion, M. Gelster, J. Helbing, V. Seyfried, and T. Baumert, Phys. Rev. A **54**, R4605 (1996).

[5] Y. Arasaki, K. Takatsuka, K. Wang, and V. McKoy, Phys. Rev. Lett. **90**, 248303 (2003).

[6] H. Stapelfeldt, E. Constant, H. Sakai, and P. B. Corkum, Phys. Rev. A **58**, 426 (1998).

[7] C. Trump, H. Rottke, and W. Sandner, Phys. Rev. A **59**, 2858 (1999).

[8] J. H. Posthumus *et al.*, J. Phys. B **32**, L93 (1999).

[9] Th. Ergler, A. Rudenko, B. F. Feuersvein, K. Zrost, C. D. Schroter, R. Moshammer, and J. Ullrich, Phys. Rev. Lett. **95**, 093001 (2005).

[10] S. A. Alnaser, B. Ulrich, X. M. Tong, I. V. Litvinyuk, C. M. Maharjan, P. Ranitovic, T Osipov, R. Ali, S. Ghimire, Z. Chang, C. D. Lin, and C. L. Cocke, Phys. Rev. A **72**, 030702 (2005).

[11] X. Urbain, B. Fabre, V. M. Andrianarijaona, J. Jureta, J. H. Posthumus, A. Saenz, A. Baldit, and C. Cornaggia, Phys. Rev. Lett. **92**, 163004 (2004).

[12] T. K. Kjeldsen and L. B. Madsen, Phys. Rev. Lett. **95**, 073004 (2005).

[13] M. Drescher, M. Hentschel, R. Kienberger, G. Tempea, C. Spielmann, G. Reider, P. Corkum, and F. Kausz, Science **291**, 1923 (2001).

[14] A. Baltuska, Th. Udem, M. Uberacker, M. Hentschel, E. Goulielmakis, Ch. Gohle, R. Holzwarth, V. S. Yakovlev, A. Scrinzi, T. W. Hänsch, and F. Krausz, Nature (London) **421**, 611 (2003).

[15] M. Drescher, M. Hentschel, R. Kienberger, M. Uiberacker, V. Yakovlev, A. Scrinzi, Th. Westerwalbesloh, U. Kleineberg, U. Heinzmann, and F. Krausz, Nature (London) **419**, 803 (2002).

[16] E. Goulielmakis *et al.*, Science **305**, 1267 (2004).

[17] B. Shan, S. Ghimire, and Z. Chang, J. Mod. Opt. **52**, 277 (2005).

[18] M. Shapiro, J. Phys. Chem. **90**, 3644 (1986).

[19] S. P. Khare, V. Saksena, and S. P. Ojha, J. Phys. B **25**, 2001 (1992).

[20] X. Chu and Shih-I. Chu, Phys. Rev. A **63**, 013414 (2000).

[21] C. Petersen, E. Peronne, J. Thogersen, H. Stapeifeldt, and M. Machholm, Phys. Rev. A **70**, 033404 (2004).

[22] N. Andersen, J. W. Gallagher, and I. V. Hertel, Phys. Rep. **165**, 1 (1988).

[23] M. Spanner, E. A. Shapiro, and M. Ivanov, Phys. Rev. Lett. **92**, 093001 (2004).