Nuclear Interference in the Coulomb Explosion of H_2^+ in Short vuv Laser Fields

Morten Førre,[1,2] Samira Barmaki,[3] and Henri Bachau[1]

[1]*Centre Lasers Intenses et Applications, Université Bordeaux 1-CNRS-CEA, 351 Cours de la Libération, F-33405 Talence Cedex, France*

[2]*Department of Physics and Technology, University of Bergen, N-5007 Bergen, Norway*

[3]*Secteur Sciences, Université de Moncton, Campus de Shippagan, 218, Boul. J.-D. Gauthier, Shippagan, New Brunswick, Canada E8S 1P6*

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We report *ab initio* calculations of H_2^+ three-photon ionization by vuv/fs 10^{12} W/cm^2 laser pulses including electronic and vibrational degrees of freedom in the Born-Oppenheimer approximation. The initial nuclear wave packet of $H_2^+(1s\sigma_g)$ is assumed to be equal to the H_2 vibrational ground state. For pulse durations longer than 10 fs, we find an unexpected modulation in the kinetic energy spectra of the correlated fragments ($H^+ + H^+$). It is shown that the structures in the spectra originate from the interference between a direct and a sequential dissociation channel. While the first channel is open even for relatively short pulses, the sequential one only opens for pulse durations longer than 10 fs. In the latter case we show that interference between the two components results in a modulated kinetic energy release spectrum in the dissociation channel $3d\sigma_g$, which is reflected in the ionization spectrum.

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Recent advances in high-order harmonic generation have enabled us to explore a new research field with fundamental issues related to light-matter interaction at the femto- and attosecond time scales [1,2]. High-order harmonic (HH) sources cover a wavelength range from the vacuum ultraviolet (vuv) to the soft x-ray radiation regime, with intensities as high as 10^{14} W/cm^2 [3], opening new research areas like nonlinear optics in the extreme-ultraviolet (xuv) regime in atoms [4,5] and molecules [6]. Femtosecond (fs) pulses are ideal to explore molecular dynamics since vibrational motion typically occurs on the fs time scale, at least for light molecules. Fundamental issues related to light-molecule interactions in intense fields whose intensity exceed 10^{12} W/cm^2 have been studied intensively in the fs regime [7,8]. Since the pioneering work of Zewail [9], visualization of the full dynamical evolution of molecular wave packets has received a lot of attention [10,11]. Coulomb explosion imaging has been shown to be efficient for real-time tracking of wave packets (to cite a recent contribution, see [12] and other references therein). Coulomb explosion (CE) also reveals coherence effects in dissociative channels [13]. Recently, wave-packet interference (WPI) has attracted a lot of attention. WPI in bound vibrational wave packets has been demonstrated in molecules by using two identical femtosecond laser pulses [14,15], and interference between two dissociative wave packets has also been observed [16,17]. What these experiments had in common is that the WPI was triggered and controlled by the delay between two successively applied pulses. Furthermore, the experiments were performed for wave packets in I_2, which have a long classical vibrational period (~305 fs). In this context, it is worth noticing that control of vibrational wave packets can be achieved with chirped or tailored fs pulses by fixing the relative phase between eigenstates of matter [18]. Many of the above studies were conducted in the near infrared (ir) (wavelength ~800 nm) or in the visible-uv regime, at the time scale of several tens of fs. In general the laser-molecule interaction is strong in this case and involves the absorption of many photons. It is noteworthy that, using vuv or xuv fields, only few photons are involved at moderate intensities (10^{12}–10^{13} W/cm^2). Also, short vuv/xuv fields open the way to exploring nonlinear effects at the time scale of the vibrational motion in light molecules. In the latter context, theoretical investigations of laser-molecule interactions have revealed new features [19,20].

In this Letter, we report on modulations in the three-photon ionization of H_2^+ by a short vuv laser pulse, related to unrevealed WPI effects in dissociative channels. The fs pulse launches a wave packet on two different potential surfaces ($2p\sigma_u$ and $3d\sigma_g$) in the molecule. Each wave packet then evolves along its respective potential curve, and finally the (same) pulse mixes the two components at a later point, inducing constructive or destructive interferences in the final wave function. Hence, the WPI occurs as a consequence of the temporal evolution of the two wave packets on different potential curves before they are superposed. This is clearly different from the scenario in [14–17] where the two wave packets propagate on common potential surfaces. This difference could possibly open the door for a new type of wave-packet interferometry at the fs time scale using single pulses. It is already known that double-pulse (two-color) nonlinear wave-packet interferometry can be a powerful tool to control interferences, and to retrieve phase and amplitude information about an optically prepared vibrational wave packet (see [21,22] for recent reviews).

Initially the H_2^+ vibrational wave packet is assumed to be equal to the fundamental state of H_2. Figure 1 shows a sketch of the time-dependent system in H_2^+. At $R \sim 2.4$ a.u. and $R \sim 3.1$ a.u., one- and two-photon absorption from $1s\sigma_g$ populate the dissociative states $2p\sigma_u$ and $3d\sigma_g$, respectively. (Note that two-photon absorption also populates the dissociative state $2s\sigma_g$). At a larger internuclear distance ($R > 5$ a.u.) $3d\sigma_g$ is strongly coupled to $2p\sigma_u$ by the laser field. Thus the state $3d\sigma_g$ is populated through two pathways, both involving two photons. Hence, in clear contrast to the experiments reported in [14–17], the WPI is triggered by one single laser pulse and therefore mainly determined by the internal degrees of freedom in the system, i.e., the quantum interference between two independent paths, and not explicitly by some preset time delay between two successive laser pulses. Note that the dissociative wave packets on the $2p\sigma_u$ and $3d\sigma_g$ potentials have similar kinetic energy release (KER) (~0.2 a.u.). This point is of crucial importance to understand the interference effect described in the following.

From fully converged (and gauge independent) *ab initio* solutions of the (Born-Oppenheimer) time-dependent Schrödinger equation (TDSE) governing the laser-molecule interaction, we have obtained the kinetic energy distributions of the molecular fragments in the dissociation and ionization channels. The kinetic energy release (KER) spectra are computed in the molecular center of mass (c.m.) reference system. The theoretical method is based on the solution of the TDSE in prolate spheroidal coordinates in a basis of stationary molecular states and includes both the 3D electronic and 1D vibrational motions.

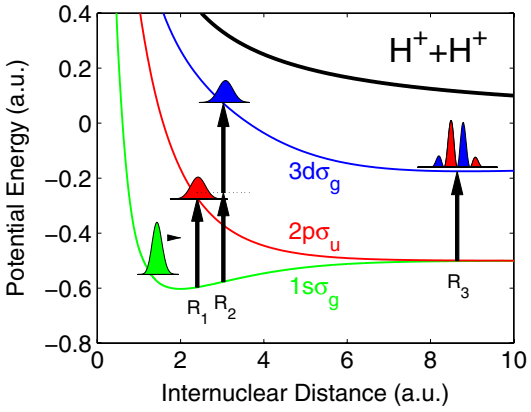

FIG. 1 (color online). Sketch of the present time-dependent three-level system in H_2^+. A wave packet created at time $t = 0$ on the $1s\sigma_g$ electronic potential surface moves rapidly towards the outer turning point accompanied by a short, soft uv femtosecond laser pulse. At $R_1 \simeq 2.4$ a.u. and $R_2 \simeq 3.1$ a.u. population is transferred coherently, via resonant one- and two-photon absorption, to the $2p\sigma_u$ and $3d\sigma_g$ surfaces, respectively. The $2p\sigma_u$ dissociative wave packet moves rapidly to $R_3 \simeq 8.6$ a.u. where a second photon pumps population to $3d\sigma_g$. Eventually a third photon ionizes the molecule and an image of the modulated $3d\sigma_g$ wave packet is reflected in the Coulomb explosion image.

For the short pulses considered here, the effect of molecular rotation could safely be neglected. Numerical details are discussed in [23]. The molecule interacted with a short (10–16 fs) laser pulse linearly polarized along the internuclear axis. The field was sinusoidal $\sim \cos(\omega t)$ with a sine-square profile, and the laser frequency ω was chosen to match the one-photon transition at R_3 as shown in Fig. 1. For the sake of simplicity, in the simulations the initial $H_2^+(1s\sigma_g)$ vibrational wave packet was set equal to the H_2 $X\,^1\Sigma_g^+(v = 0)$ (ground) state. However, we would like to emphasize that the mechanism outlined in this Letter is also present for other choices of initial conditions and pulse characteristics.

Figure 2 (upper panel) shows the KER of the nuclear fragments in the CE channel ($H^+ + H^+$) that follows from three-photon ionization of the H_2^+ wave packet by a short vuv fs laser pulse. The lower panel displays the corresponding results for the electron. The central frequency and intensity of the laser field were $\omega = 0.32$ a.u. and $I = 1 \times 10^{12}$ W/cm^2, respectively. Results for varying (total) pulse durations between 10 and 16 fs are displayed in the figure. The KER of the protons generally shows a characteristic multipeak structure with two main peaks located at the proton energies ~0.35 and ~0.4 a.u., respectively. A notable exception is the case with the shortest pulse (10 fs) where the spectrum contains only one peak. In accordance with the principle of conservation of energy, the KER of the escaping electron (necessarily) exhibit a similar oscillatory pattern than the proton distributions, i.e., there is a one-to-one correspondence between the peaks in the proton and electron spectra. Note that we have extended the x-axis range to include some negative values of the electron energy in order to clearly identify the two (main) peaks in the electron spectra.

Figure 3 shows the KER in the $3d\sigma_g$ dissociative channel ($H^* + H^+$) for the same cases than in Fig. 2. Again, for the longest pulses the spectra contain two clear peaks. Although there are differences in the actual shapes of the KER spectra in the $H^+ + H^+$ (CE) and the $H^* + H^+$ ($3d\sigma_g$) channels, they clearly resemble each other in the sense that they are both modulated. This simply suggests that the modulations in the ionization spectra are signatures of the population dynamics that has been going on in the dissociating H_2^+ channels ($1s\sigma_g$, $2p\sigma_u$, and $3d\sigma_g$) during the pulse. In this sense, one may say that the (single) pulse acts both as a pump and probe.

The modulation in the spectra may be interpreted as a pure WPI effect. To see this, we consider a simple model in which the initial vibrational wave packet moves out along the $1s\sigma_g$ electronic potential surface towards its outer turning point. On its way, it passes by the positions R_1 and R_2 where additional wave packets are launched onto the excited $2p\sigma_u$ and $3d\sigma_g$ electronic potential surfaces, respectively, via resonant one- and two-photon absorption. The $2p\sigma_u$ dissociative wave packet then moves rapidly towards the one-photon resonance at R_3. Here, a fraction of

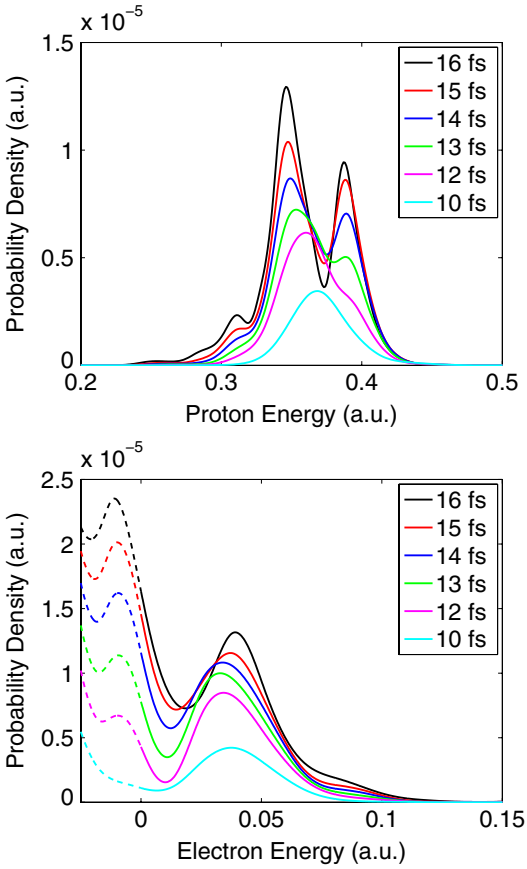

FIG. 2 (color online). Ionization of an H_2^+ wave packet by a femtosecond laser pulse of central frequency $\omega = 0.32$ a.u. and intensity $I = 1 \times 10^{12}$ W/cm^2. The initial vibrational wave packet at $t = 0$ is assumed to be of Franck-Condon type [24]. Upper panel: The (center of mass) kinetic energy release (KER) spectrum of the nuclei after full fragmentation (ionization followed by Coulomb explosion of the nuclei) of the molecule. For comparison, calculations for different (total) laser pulse durations, 16, 15, 14, 13, 12, and 10 fs, are shown. Lower panel: The corresponding KER of the electrons in the continuum. For reasons indicated in the text, a part of the spectrum corresponding to a situation where the electron remains bound to the one and/or the other nucleus (negative electron energy) has been included in the figure (dashed lines).

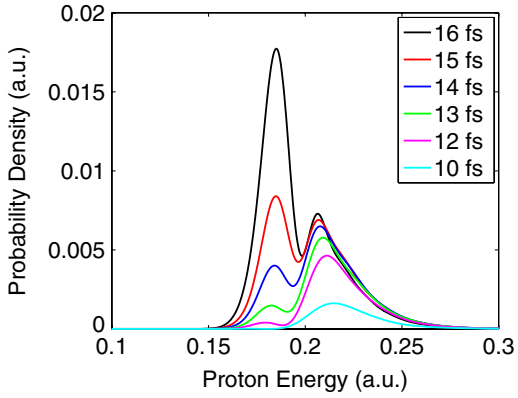

FIG. 3 (color online). As Fig. 2, but the KER of the protons in the dissociative $3d\sigma_g$ channel (see Fig. 1).

it is transferred to $3d\sigma_g$ and added coherently to the wave packet that was initially launched at R_2. Now, the two pathways, sequential one-photon absorptions (at R_1 and R_3) and direct two-photon absorption (at R_2), interfere and create a modulated wave packet on the $3d\sigma_g$ potential surface. Finally, a third photon ionizes the molecule and an image of the modulated wave packet is reflected in the ionization channel. Now, suppose the movement of the wave packets on the two independent paths from R_1 to R_3 has given rise to a time delay ΔT between the two components, then the addition of the two in the $3d\sigma_g$ channel leads to a modulation of the form $|1 + Ae^{iE\Delta T}|^2$ in the energy distribution. Here, $Ae^{iE\Delta T}$ represents the relative amplitude between the two wave packets and E is the KER. To estimate ΔT we have solved the classical equations of motion for a particle starting out in the position R_1 with an initial velocity given by the (group) velocity of the wave packet. Assuming that the transitions at R_1, R_2, and R_3 occur instantaneously one may calculate the ΔT for the classical movement along the two different possible paths from R_1 to R_3. For the particular case investigated here, we find the time delay to be about 130 a.u. ($\sim$3 fs), which corresponds to a separation of about 0.04–0.05 a.u. in energy between two successive peaks in the KER spectrum. This value is compatible with the structures in Figs. 2 and 3, although due to the limited energy spreading of the wave packet, the peaks (may) appear somewhat closer. Note that we have assumed in the above model that the vibrational wave functions $\psi^v_{2p\sigma_u}(E)$ and $\psi^v_{3d\sigma_g}(E)$ are identical. In fact, at large internuclear distance, they both behave like $\sim \sin(kR + \ldots)$ [where $k = (2\mu E)^{1/2}$, μ being the reduced mass], but their amplitude differs by a molecular phase factor $e^{i\delta(k)}$. We have checked that including this factor in the interference term does not modify our conclusions. Now, the absence of modulation for shorter pulses ($\lesssim$10 fs) may be understood from the fact that the $2p\sigma_u$ wave packet never reaches the resonance at R_3 during the pulse.

Owing to the above considerations, the interference effect should be observed for other choices of the initial vibrational wave packet. It is even more clear when the initial state is stationary. Figure 4 shows the case of $H_2^+(v = 3)$ absorbing two photons to $3d\sigma_g$. The KER of the protons has a well pronounced structure with a minimum close to zero at $E = 0.2$ a.u. We also show in Fig. 4 a case were the dipole coupling between $2p\sigma_u$ and $3d\sigma_g$ is arbitrarily cancelled for $R > 5$ a.u. Now a single peak appears, positioned at $E = 0.2$ a.u., and it represents in fact the $3d\sigma_g$ wave packet created through the direct two-photon absorption process at R_2.

Note that the two other important dissociative channels, $2p\sigma_u$ and $2s\sigma_g$, that are also populated throughout the pulse, do not expose similar oscillatory behavior. Here the key role of $3d\sigma_g$ rely on the fact that we have tuned the

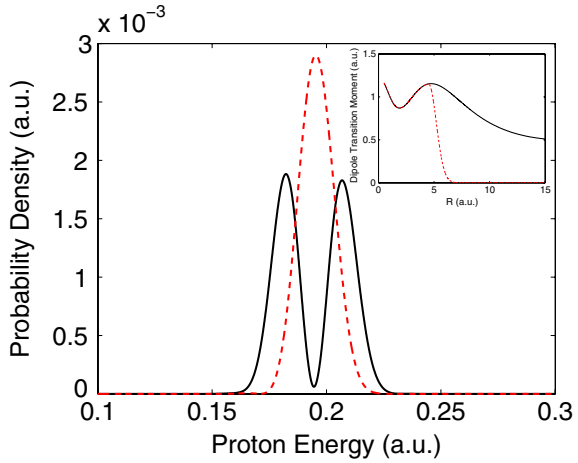

FIG. 4 (color online). KER of the protons in the dissociative $3d\sigma_g$ channel from the dissociation of the stationary state $1s\sigma_g(\nu = 3)$ by a 27-cycle ($T = 13$ fs) laser pulse with $\omega = 0.317$ a.u. and $I = 1 \times 10^{12}$ W/cm^2. The dashed red curve shows the corresponding (artificial) result one obtains when the dipole transition moment between the $2p\sigma_u$ and the $3d\sigma_g$ electronic states is turned off (a priory) at large internuclear distance (as indicated in the inset).

laser frequency so that there are two possible pathways that the population may follow in order to end up in this particular final channel. The choice of another frequency could possibly create a similar modulated wave packet on another dissociative potential surface. On the other hand, the $3d\sigma_g$ potential surface is somewhat special as it has a minimum at $R \simeq R_3$ and a strong dipole coupling with $2p\sigma_u$, and therefore makes it a clear candidate for exposing this kind of behavior. Also it is worth to note that similar effects should be observed in H_2.

In conclusion, we have calculated three-photon CE ionization of H_2^+ in a short vuv laser pulse in the multiphoton absorption regime, at moderate laser intensity (10^{12} W/cm^2). The KER spectra reveal interference structures that are directly related to the population dynamics and phase relationships in two dissociative channels. The effect is also present at lower intensities, i.e., the lower limitation in the context of an experiment would be given by the measurement statistics. With ultrashort pulses ($\lesssim$10 fs) the three-photon ionization process occurs at short internuclear distances and includes resonant two-photon transition to $3d\sigma_g$. At longer pulse durations a two step process involving the (intermediate) $2p\sigma_u$ dissociative state comes into play, leading to interference in the $3d\sigma_g$ dissociative channel, which is reflected in the CE spectrum. In the present work we have used a single Fourier-transform-limited pulse. The use of chirped pulses may offer interesting perspectives regarding the control of interference phases, thus opening a way to switch between constructive and destructive interferences in dissociative channels. Although here we have only considered one specific situation in the hydrogen molecular ion, we expect similar population dynamics to occur in other (molecular) systems. Owing to the present interest on molecular dynamics on the fs time scale in the vuv and xuv regime, using new laser sources (like harmonics or free electron lasers), we believe that the proposed WPI effect may be measured in the near future. Indeed, considering the laser parameters used in the calculations, i.e., 10–16 fs pulse duration and vuv fields of moderate intensity, experiments could be realized with harmonic generation sources, which are now developed worldwide using Ti:sapphire lasers.

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