Asymmetric Electron-Nuclear Dynamics in Two-Color Laser Fields: Laser Phase Directional Control of Photofragments in H_2^+

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Exact non-Born-Oppenheimer numerical solutions of the time-dependent Schrödinger equation for the 1D H_2^+ molecule in an intense, two-color ($\omega + 2\omega$) laser field have been obtained. Both electron and proton kinetic energy spectra show spatial, correlated, asymmetric distributions. The calculated spectra exhibit the same unusual correlations as in experiments, in which both positively charged nuclear fragments and negatively charged photoelectrons were preferentially emitted in the same direction. The above asymmetries of photoemission of electrons seen in our quantum simulation are interpreted in the framework of a quasistatic tunneling model.

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Laser control of nuclear motion in molecules is a growing area of research due to the ever improving laser technology making available laser pulses with variable (and controllable) amplitude and phase. Thus various coherent control scenarios have been envisaged to control photochemical products in chemical reactions by coherent superpositions of electronic or (and) nuclear states [1]. In particular, the simple superposition of a field of frequency ω and its second harmonic 2ω, $\omega + 2\omega$ scenarios, leads to control of the angular distributions of the photoelectron in the ionization processes [2,3] or to the directional control of photocurrents in quantum wells [4] and in semiconductors [5]. Thus we have shown previously that by using $\omega + 3\omega$ and $\omega + 2\omega$ coherent superpositions of laser pulses, one can control ionization [6] and also enhance high order harmonic generation [7] in the simplest molecule H_2^+.

Previous experimental attempts to control dissociative ionization using a $\omega + 2\omega$ scenario were reported for H_2 and HD molecules [9,10]. Strong directional asymmetries of positively charged nuclear fragments and ionized electrons were found. Unexpectedly, both positively charged nuclear fragments and negatively charged electrons were preferentially emitted in the same direction, which seemed to be "counterintuitive," since for the case of the most asymmetric combined electric field [which occurs when $\phi = 0$ or $\phi = \pi$, see inset in Fig. 1(a)], one might expect that positively charged nuclei will be preferentially pulled in the direction to which the maximum field points, whereas the negatively charged electron would accelerate in the opposite direction (i.e., down field), contrary to what the experiment shows. So far, in our opinion, no theoretical, satisfactory explanation of this puzzle has been provided. It was assumed that the electrons behave "normally," and the anomalous behavior was attributed to more complex nuclear effects. Previous theoretical calculations relevant to this issue were performed either in the framework of static nuclei [6] or were based on only two-electronic state models of H_2^+ [11] (i.e., without ionization). We explain these unusual experimental results in two ways: first, by solving the complete dynamic time-dependent Schrödinger equation (TDSE) for H_2^+ we computed the kinetic energy spectra of electrons and protons from our final wave function. We observe the same kind of correlated asymmetries as seen in experiment, i.e., we see a preferential emission of electrons and protons in the same direction. For $\phi = 0$ we observe the counterintuitive emission of electrons in H_2^+, i.e., more electrons ionizing towards the positive field maximum [see inset in Fig. 1(a)]. However, in experiments electrons ionizing

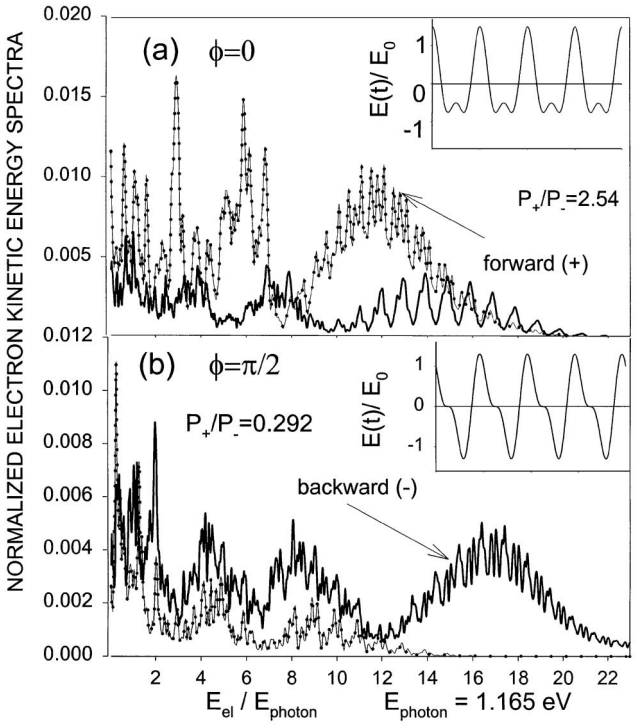

FIG. 1. Photoelectron kinetic-energy (ATI) electron spectra for non-Born-Oppenheimer H_2^+ in the two-color (1064 nm + 532 nm) field, shown in the insets, with $I_0 = 4.4 \times 10^{13}$ W/cm^2, $f = 0.5$. Solid thick line: backward ($z < 0$) electron; dotted, thin line: forward ($z > 0$) electron. (a) $\phi = 0$, (b) $\phi = \pi/2$.

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from H_2 and from H_2^+ are not distinguished, and more measured electrons originate from H_2 than from H_2^+ [9,10]. Since we expect that the asymmetry of electrons ionizing from H_2 will be similar to that in a hydrogen atom, we have also calculated the electron spectra from the H atom. We observe similar electron anomalous asymmetries in the H-atom above threshold ionization (ATI) electron spectra as in H_2^+. Next, we use a quasistatic tunneling model to interpret those asymmetries. We perform classical simulations of electron trajectories escaping the H atom after tunneling takes place. The trajectories were initialized with the velocity $v = 0$ at the moment when the electron has tunneled through the potential barrier. We include the electron-proton interaction after tunneling in our simulations. We show that this simple model explains well the asymmetries seen in our complete quantum calculations in H and H_2^+.

We have solved numerically the complete, three-body, 1D, TDSE with both electronic and nuclear degrees of freedom included,

$$i\,\frac{\partial\psi(z,R,t)}{\partial t} = H(z,R,t)\psi(z,R,t)\,, \qquad (1)$$

where R is the internuclear distance, z is the electron position with respect to the two protons center of mass, and $H(z,R,t)$ is the three-body Hamiltonian for H_2^+ [12] in a laser field $E(t)$. We have used laser pulses of total duration $t_p = 95.5$ fs (27 cycles of the YAG laser), at wavelengths $\lambda = 1064$ and 532 nm. The two-color electric, laser electric field used in our simulation, has the following form:

$$E(t) = E_0(t)[\cos(\omega t) + f\cos(2\omega t + \phi)], \qquad (2)$$

where $E_0(t)$ is the field envelope (we use 17.7 fs rise and fall), and ϕ is the phase, which can be controlled in the experiment. We set $f = 0.5$, since it gives the largest asymmetry in $E(t)$; see the inset in Fig. 1(a). The initial vibrational wave function of H_2^+, at $t = 0$, was assumed to be a coherent superposition of H_2^+ vibrational states, equal to the vibrational $v = 0$ function of H_2. This is equivalent to assuming that during the ionization of H_2 the nuclei remained frozen and direct vertical Franck-Condon transitions from H_2 to H_2^+ take place [12]. The resulting populations in H_2^+ have a broad peak around $v = 3$, extending up to $v = 9$, which is close to population distributions occurring in experiment after the ionization of H_2.

We have obtained numerically the time evolution of the wave function $\psi(z,R,t)$ using the split-operator method and a wave function splitting technique [12], which allows one to recover the probability flux lost in absorbing boundaries, thus allowing us to compute the complete electron kinetic energy spectra ATI, and proton kinetic energy. More specifically, our technique gives us the internal wave function at the final time $t_f = 42$ cycles $> t_p$, $\psi_{\rm in}(z,R,t_f)$ (defined in z values close to the nuclei, $|z| < 512$ a.u., which was absorbed during the computation), and asymptotic wave functions: $\varphi_+(p,R,t_f)$ and $\varphi_-(p,R,t_f)$ [12], for electrons moving in positive and negative z directions, respectively, where p is the electron momentum. The normalized ATI electron spectra, displayed in Fig. 1, were obtained by integrating $|\varphi_\pm(p,R)|^2$ over R and multiplying by a Jacobian dp/dE. The asymmetric proton spectra were calculated by projecting the internal wave function $\psi_{\rm in}(z,R,t_f)$ on the ground state hydrogenic electron wave function $\psi_{\rm H}(z \mp R/2)$, each representing the electronic states, with the electron localized at $z = \pm R/2$, respectively. Thus we obtain two R-dependent functions:

$$\psi_\pm(R) = \int_{-\infty}^{\infty} \psi_{\rm H}(z \pm R/2)\,\psi_{\rm in}(z,R,t_f)\,, \qquad (3)$$

where $\psi_+(R)$ represents the proton moving up the maximal field (forward, $z > 0$) shown in the inset of Fig. 1(a) and vice versa. Next the Fourier transform $\chi_\pm(p_R)$ (where p_R is the proton momentum) of the asymptotic part [12] of $\psi_\pm(R)$ was calculated. Thus $|\chi_\pm(p_R)|^2 dp_R/dE$ represents the forward (backward) kinetic energy spectra of nuclear fragments, which are displayed in Fig. 2. The intensity of the 1064 nm laser used in our two-color calculations was $I_0 = cE_0^2/8\pi = 4.4 \times 10^{13}$ W/cm^2 and the 562 nm laser had intensity 1.1×10^{13}, giving the maximum field (at $\phi = 0$) $(1 + f)E_0 = 1.5E_0$ (such a peak field is reached with one laser having intensity 10^{14} W/cm^2). Two particular relative phases ϕ were chosen: $\phi = 0$ [Figs. 1(a) and 2(a)] and $\phi = \pi/2$ [Figs. 1(b) and 2(b)]. The corresponding combined electric fields are shown in insets in both Figs. 1(a) and 1(b). We write in each figure the value of the forward/backward probability P_+/P_-, obtained by calculating the areas under dotted and solid lines, respectively, in each figure.

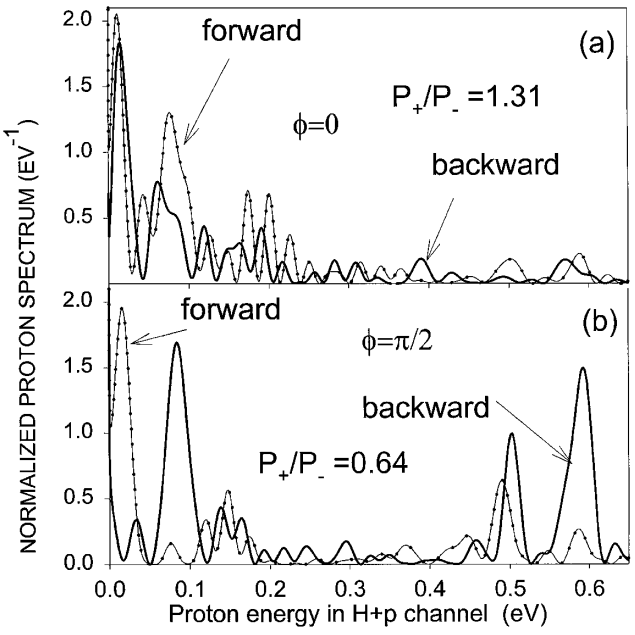

FIG. 2. Proton kinetic energy spectra in the p + H channel calculated with the same laser field as in Fig. 1. Solid thick line: backward ($z < 0$) proton; dotted thin line: forward ($z > 0$) proton. (a) $\phi = 0$, (b) $\phi = \pi/2$.

For $\phi = 0$ (case of largest asymmetry in the combined field $E(t)$], the electrons ionize preferentially forward ($P_+/P_- = 2.54$), i.e., up the maximum field, contrary to simple classical expectation that a negatively charged particle should preferentially accelerate down the maximum field. The protons, however, behave normally: They move up the maximum field ($z > 0$) yielding ($P_+/P_- = 1.31$), i.e., in the same direction as electrons. Thus our calculations reproduce well, for $\phi = 0$, correlations seen in experiment [9,10] ($P_+/P_- = 1.3, \pm 0.1$, for protons, see Fig. 3(a) in Ref. [9]), i.e., the preponderance of electrons and ionizing electrons and dissociating protons, in the same direction, with $P_+/P_- > 1$ for electrons and protons.

The $\phi = \pi/2$ case, Figs. 1(b) and 2(b), corresponds to a "symmetric" electric field. Thus one would expect symmetric ionization; however, one should note that, contrary to the case $\phi = 0$, now, the electric field is asymmetric around the field maxima. The numerical ATI spectra, Fig. 1(b), show a strong forward-backward asymmetry, with the backward ($z < 0$) electron yield being dominant, yielding $P_+/P_- = 0.29 < 1$. Such strong asymmetries, for $\phi = \pi/2$, were seen in ATI spectra of electrons ionizing from atoms [2,3]. The corresponding proton spectra show also the backward preponderance, with $P_+/P_- = 0.64$. Clearly, our calculations reproduce well the intriguing correlated emission of protons and electrons seen in the experiment, for both phases, $\phi = 0$ and $\phi = \pi/2$.

In order to check whether these unexpected directional asymmetries of photoionized electrons are specific to molecules, as well as to establish the asymmetry of electrons ionizing from H_2 (so far, no experiment was done with H_2^+) we have solved the time dependent Schrödinger equation for a 1D H atom in the same two-color laser field, for $I_0 = 0.44 \times 10^{14}$ and for $I_0 = 10^{14}$ W/cm^2. For the latter, we fall completely, with the 1064 nm laser, into the tunneling regime (Keldysh parameter $\gamma = \sqrt{I_p/2U_p} = 0.93$). Table I summarizes P_+/P_- the forward/backward ionization probabilities P_+/P_-, in 1D H atom and in H_2^+, for the relative phases $\phi = 0$ and $\phi = \pi/2$. We conclude that asymmetries in H-atom electrons exhibit similar anomalous behavior to that in H_2^+, i.e., a preponderance of the electrons are in the forward direction, $z > 0$, for $\phi = 0$. We provide, in the following, a simple explanation of these anomalies using the quasistatic tunneling model. In this model ionization occurs in two steps. In the first, the electron ionizes the H atom with a tunneling rate $R_{\text{tun}}(E)$ that depends on the instantaneous field $E(t)$ [13]. Second, the electron moves in the laser field only, as a classical particle, starting at rest at the tunneling moment t_0 at $z = z_0$, determined by the condition $V(z, t_0) = -I_p$, where $V(z,t) = -(z^2 + 1)^{-1/2} + zE(t)$ and where $I_p = 0.6697$ a.u. is the ionization potential of our 1D H atom. By solving the Newton equation of motion in the two-color laser field only, Eq. (2), with the initial velocity $v(t_0) = 0$, and position $z = z(t_0) = z_0$, we get the following solution for the electron velocity $v(t)$:

$$v(t) = v_d(t_0) - \frac{E_0}{\omega}\left[\sin(\omega t) + \frac{f}{2}\sin(2\omega t + \phi)\right], \tag{4}$$

$$v_d(t_0) = \frac{E_0}{\omega}\left[\sin(\omega t_0) + \frac{f}{2}\sin(2\omega t_0 + \phi)\right], \tag{5}$$

where v_d is the electron drift velocity. After slow turn-off of the pulse the oscillatory term in (5) averages out to zero and then the final electron velocity of the ionized (at $t_{\text{final}} \gg t_0$) electron coincides with the drift velocity $v_d(t_0)$. Thus the drift velocity and tunneling rate R_{tun} [2,13] at tunneling time t_0 determine the ATI spectrum of electrons, in a model which neglects the Coulomb attraction by the proton. Because of the exponential behavior of the tunneling rate $R_{\text{tun}}(E)$, only values in a small fraction of a cycle interval around the field maximum determine the final electron velocity distribution. This simple model explains very well the case of a symmetric electric field, $\phi = \pi/2$. We have plotted in Fig. 3(b) the drift velocity v_d [given by Eq. (5)] and the electric field $E(t_0)$ as a function of the tunneling time t_0, for the relative phase $\phi = \pi/2$. Because of the symmetry of the field, the tunneling occurs, with the same probability at field minima and maxima, i.e., at both sides of an ion. Note that the corresponding drift velocity, $v_d = -0.375E_0/\omega = -0.467$ a.u., is negative in the large intervals around the field maximum and minimum [see two larger circles in Fig. 3(b)] and is the same for both. Thus the electrons tunneling from each side of the proton will preferentially move backward, i.e., in the $z < 0$ direction, in agreement with our quantum calculations; Fig. 1(b) and Table I.

In the case of the phase of $\phi = 0$ the electric field is two times stronger in the positive direction, therefore we expect the tunneling to occur, predominantly, at one side of the nucleus, at negative z_0. At first sight one might, therefore, expect the preponderance of the backward electrons, but by repeating the previous analysis, based on the behavior of the drift velocity as a function of t_0, we note that now the field reaches a maximum at $t_0 = 0$, and v_d is antisymmetric around the field maximum, i.e., $v(-t_0) = -v(t_0)$. This means that, by counting trajectories initialized at various t_0 around the field maximum, we should observe the same number of trajectories ionizing forward and backward, because of the symmetry of the electric field $E(t)$ around the field maximum. Summarizing, the standard

TABLE I. Values of forward/backward probabilities P_+/P_- for electrons and protons in H_2^+, for electrons in quantum and classical H atom. We used $I_0 = 0.44 \times 10^{14}$ W/cm^2, except as otherwise stated.

ϕ	Electrons in H_2^+	Protons in H_2^+	H	H (10^{14})	Classical (10^{14})
0	2.538	1.313	4.715	3.494	3.212
$\pi/2$	0.299	0.643	0.3567	0.0948	0.218

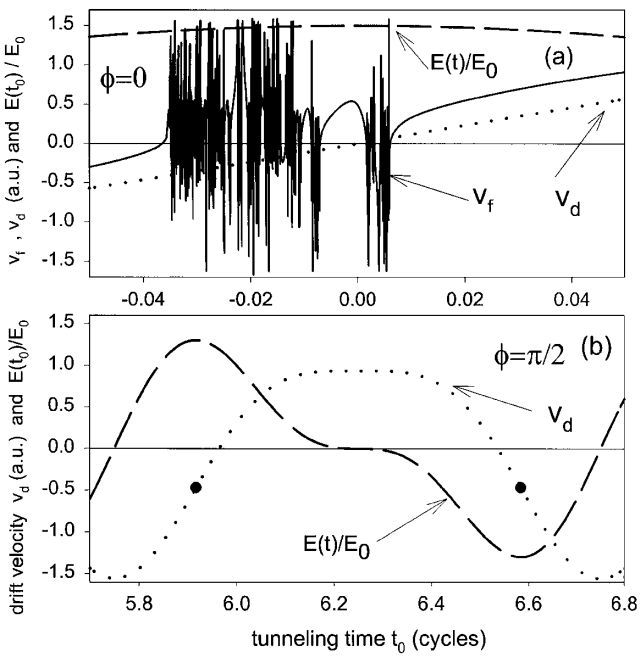

FIG. 3. Laser electric field $E(t)/E_0$ (dashed line), and the corresponding drift velocity v_d (dotted line), as a function of the tunneling time t_0 for (a) the relative phase $\phi = 0$; v_f (solid line) are final velocities of ionized electrons obtained from numerical solution of 1D classical of motion including the Coulomb attraction from parent ion; (b) $\phi = \pi/2$, only $E(t)/E_0$ and v_d are plotted. The two larger circles indicate the values of v_d at times when the field reaches a maximum and minimum.

tunneling model predicts no forward/backward asymmetry [2,13], for $\phi = 0$, contrary to what we obtain by solving the TDSE [see Fig. 1(a) and Table I]. We obtain a strong preponderance of forward electrons for both molecular and atomic electrons.

We show, in the following, that the asymmetry (in the $\phi = 0$ case) arises from the Coulomb attraction by a parent ion. The tunneling probability is greatest for the electrons with zero drift velocity, and thus the electrons having small negative drift velocity will be attracted by the core and finally will preferentially ionize forward ($z > 0$) instead of drifting backwards (i.e., down field). Specifically, we have solved numerically the classical equation of motion for $v(t)$ using the exact potential $V(z, t)$ which includes the Coulomb potential of the proton. We have launched 8000 trajectories, with equally spaced t_0 values around the field mximum in the interval $[-0.1{:}0.1]$ cycles (of a YAG laser), and calculated the final velocity (averaged over the last cycle) of the ionized electron, after 25 cycles of classical simulation. Each trajectory was initialized at $z = z_0$ with $v(t_0) = 0$. Figure 3(a) shows final velocities of electrons as a function of tunneling time t_0. These final velocities are compared with (dotted line) the final velocities [equal to v_d, given by (5)] expected from the standard tunneling model, in which electron-ion interaction is neglected. Clearly, many more trajectories end in the forward direction ($z > 0, v_{\text{final}} > 0$). We have counted separately all trajectories moving forward and backward, weighting them by the tunneling rate $R_{\text{tun}}[E(t_0)]$, using the following classical definition of ionization probability $dP = dt_0 R_{\text{tun}}[E(t_0)]$. For $I_0 = 10^{14}$ W/cm^2, $\phi = 0$ we thus get $P_+/P_- = 3.21$. This classical result compares very well with $P_+/P_- = 3.49$ obtained from quantum calculations for the H atom. Table I summarizes all our calculations of P_+/P_- for electrons and protons. By comparing these coefficients for two intensities, $I_0 = 0.44 \times 10^{14}$ and $I_0 = 10^{14}$, for $\phi = 0$, we observe that the electron asymmetry is less for higher intensities. This suggests that the asymmetry disappears for higher intensities ($\gamma \ll 1$), as predicted by the standard tunneling model [2,13]. As a general rule, asymmetric electrons and protons are much slower for $\phi = 0$ than for $\phi = \pi/2$, as in Fig. 1(b) which shows electrons with energies considerably higher than for $\phi = 0$, Fig. 1(a). This behavior of electrons is very well explained by the tunneling model, which predicts that for $\phi = 0$ fast electrons are much less likely, since near the field maximum the drift velocity is zero, whereas for $\phi = \pi/2$, the drift velocity at field maximum is $v_d = -0.375E_0/\omega$. Similarly, fast protons are favored for $\phi = \pi/2$ and most are asymmetric. The proton asymmetries are strongly correlated with electron asymmetries for both phase values. For $\phi = 0$ the proton asymmetries are such as expected from the bond softening mechanism: The stronger positive electric field displaces the electron cloud down the field, thus favoring slow proton production, by dissociation, up the field. For $\phi = \pi/2$, the rapid change of the electric field (occurring when $E = 0$), induces nonadiabatic effects, which lead to the asymmetric dissociation, involving fast protons.

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