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Attosecond control of ionization and high-order harmonic generation in molecules

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Photoionization and high-order harmonic generation (HHG) in molecular systems under the action of combined infrared femtosecond (fsec) and ultraviolet attosecond (asec) laser pulses are investigated numerically for a one-dimensional non-Born-Oppenheimer H_2^+ ion. It is shown that punctual ''turn-on'' of an asec pulse can trigger the ionization process, which in turn leads to significant *enhancement* of HHG. The conversion efficiency of HHG can exceed the one obtained from a single fsec pulse by several orders and can be as high as 10^{-2} by controlling the recolliding electron responsible for the maximum order in HHG. The HHG spectrum becomes broader and quasicontinuous near the cutoff. This spectrum can be used to synthesize new single x-ray ultraviolet pulses as short as 250 asec.

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High-order harmonics are currently used in a number of applications in different fields of science and technology. It is a promising way to generate coherent x-rays in the ''water window'' (4.4–2.3 nm) and to produce asec extreme ultraviolet (XUV) pulses (see, for example, Refs. [1–4]). Recently, first experimental results on the production and measurement of a 650-asec pulse were reported [5]. This asec pulse is in the soft-x-ray spectral range and was obtained using high-order harmonic generation(HHG). Another approach for generating asec pulses is stimulated Raman scattering (SRS). The asec pulses generated by SRS method usually are in the UV range, and consist of a single or a half oscillation [6–11]. In principle, asec pulses can be focused to achieve the intensities that are comparable to the conventional Ti:sapphire lasers, i.e $I_{\mathrm{asec}} \sim 10^{14}$ W/cm^2 [12,13]. This opens up new possibilities for studying and controlling electron dynamics in atoms and molecules in asec time scale [14–16], and is expected to have major impact on the new science of laser control and manipulation of molecules [17].

Controlling HHG has become an active research area. The physics of this is based on the quasiclassical ''three-step model'' [18] that consists of the following:

(i) An electron leaves an atom and enters the ionized continuum at time t_0 (birth time) with initial velocity $v_0 = 0$,

(ii) The free electron then is accelerated by the strong electric field and gains energy.

(iii) The electron is driven back into the vicinity of the parent ion or a neighboring ion in a molecule [19], then it may recombine to the ground state to emit a high-frequency photon at time t_1 (recombination time). By manipulating the different steps of this dynamical process, one can, in principle, control HHG. Several schemes for HHG control have been suggested (see Refs. [20–23] and references therein). These schemes alter the trajectory of the electron in the continuum (the second step) by using additional static electric, magnetic or alternating electric (two- or three-color) fields. The effect of the additional field on the ionization (the first step) is of secondary importance.

In this paper we suggest and investigate a different method for controlling ionization and HHG. The physics of our method is the following. It is well known that the maximum cutoff in HHG is achieved when a rigorous relation between t_0 and t_1 is satisfied [24] [for example, when $v_0 = 0$, $\omega_l t_0 = 0.1\pi$, and $\omega_l t_1 = 1.4\pi$ (ω_l is the frequency of the driving field)]. Then by using an intense asec pulse, one can precisely trigger the ionization process and therefore achieve maximal HHG enhancement. Our simulations show that, this way, we can enhance HHG by several orders and achieve HHG efficiency as high as 10^{-2}. [Rigorously, a conversion efficiency can only be specified, when macroscopic propagation effects are included. In this paper we consider HHG in a single molecule, so the efficiency is understood as the ratio between the intensities of high-order and the fundamental harmonics].

Our investigation is based on the exact (non-Born-Oppenheimer) solution of the one-dimensional three-body Schrödinger equation for the H_2^+ ion in the field of strong, ultrashort linear polarized laser pulses,

$$i\frac{\partial \psi(z,R,t)}{\partial t} = \left[-\beta \frac{\partial^2}{\partial z^2} - \frac{1}{m_p}\frac{\partial^2}{\partial R^2} + \frac{1}{R} + V_C(z,R) + \kappa z[E_l(t) + E_{\mathrm{asec}}(t)] \right] \psi(z,R,t), \quad (1)$$

where

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

$\beta = (2m_p+1)/4m_p$, $\kappa = 1 + 1/(2m_p+1)$, R is the internuclear distance, z is the electron position with respect to the nuclear center of mass; E_l and E_{asec} are electric fields of infrared (IR) fsec, and UV asec pulses (both polarize along the z axis); and m_p is the proton mass (atomic units are used throughout). The electric fields are given by $E_j(t) = -(1/c)(\partial A_j/\partial t)$, where

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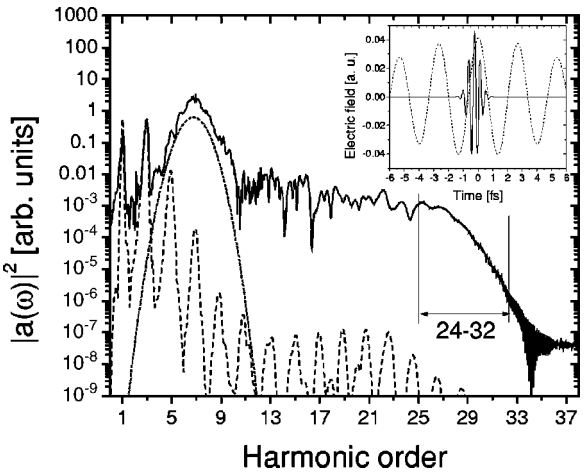

FIG. 1. HHG generated by two laser pulses when $\tau_{del}\omega_l = -0.2\pi$ (solid line). The dashed line shows HHG produced by a single 800-nm-fsec pulse and the dotted line shows the spectrum of an asec pulse. The inset shows electric fields of the two pulses.

$$A_j(t) = -\frac{cI_j^{1/2}}{\omega_j} f_j(t-\tau_j)\sin[\omega_j(t-\tau_j)], \quad j = l, \text{asec}. \quad (3)$$

ω_j and I_j are frequencies and intensities, and $f_j(t)$ and τ_j are field envelopes and the peak positions of pulses, respectively. Note that, in the ultrashort pulse limit, the definition of electric fields via vector potentials as in Eq. (3) is accurate as it ensures the condition $\int_{-\infty}^{\infty} E(t)dt = 0$. In the notation (3) the delay time of the asec pulse with respect to the IR fsec pulse is $\tau_{del} = \tau_{\text{asec}} - \tau_l$. The method of solution of Eq. (1) is described in detail in Ref. [25], with applications in Ref. [26]. We chose a molecular ion rather than an atom because of larger radiative couplings in the former leading to enhanced ionization [charge resonance enhanced ionization(CREI)] exceeding that of the parent atoms by several orders of magnitude [19,25]).

In our investigation we consider the H_2^+ ion that is in the initial stationary vibrational state $v = 2$ [26]. We use two laser pulses, both having Gaussian pulse envelopes. The 800-nm, 10-fsec driver pulse has the peak intensity $I_l = 6 \times 10^{13}$ W/cm^2. The UV asec pulse (called the "controlling" pulse) has the peak intensity $I_{\text{asec}} = 7.5 \times 10^{13}$ W/cm^2. Unless specified, the duration of the UV pulse is 0.6 fsec, and its wavelength is 115 nm, near resonant with the (HOMO-LUMO) at the CREI distance $R_c \simeq 7$ a.u., where maximum ionization occurs [25].

In the inset of Fig. 1, we plot the electric fields of the two pulses for the case $\tau_{del} = -0.1T$ ($T = 2\pi/\omega_l$ is an optical period of driver pulse). It can be seen that the UV asec pulse remarkably modifies the field of the driver pulse within a half optical period around τ_{asec} but leaves other periods untouched. This clearly indicates the differences between our method and previous two-color schemes [20–23]. In the latter cases the two laser fields usually have the same durations that are much longer than the optical periods T. The modifications of the driving field are repeated each period over the whole pulse duration. The delay time between the two pulses, when it is short, is not an important issue.

First, we have calculated the HHG spectra (the square of the dipole acceleration $|a(\omega)|^2$) produced by the two laser pulses (called the "combined" spectrum) at different time delay τ_{del}. We have changed the phase $\varphi = \tau_{del}\omega_l$ with step $\Delta\varphi = 0.2\pi$ within the region $-\pi \leqslant \varphi \leqslant \pi$ around the central peak of IR fsec pulse and followed the changes in the combined HHG spectrum. [In Fig. 1 we plot the combined HHG spectrum at $\varphi = -0.2\pi$. For comparison we also plot the HHG spectrum produced by the single 800-nm fsec-pulse and the spectrum of the UV asec pulse.] We observe that the combined HHG spectra, in general, have higher cutoff (as compared to the spectrum produced by a single fsec driver pulse alone). It is important to note that the *extension* of cutoff into the high-energy region is not due to additional kinetic energy that electron can gain from the UV asec pulse. Since the ponderomotive energy U_p is given by

$$U_p = \sum_{j=l,\text{asec}} U_{p,j} = \sum_{j=l,\text{asec}} \frac{I_j}{4\omega_j^2}, \quad (4)$$

and in our investigation $I_{\text{asec}} \simeq I_l$ but ω_{asec} is seven times higher than ω_l, therefore $U_{p,\text{asec}}$ is ~ 50 times less than $U_{p,l}$. The UV asec pulse alone does not produce a HHG spectrum. The *extension* of cutoff into the high-energy region is also not due to the broadband spectrum of the asec pulse. As can be seen from Fig. 1, this spectrum completely falls off at the 13th harmonic, while the combined spectrum exhibits a wide plateau with a clear cutoff at the 25th harmonic. Besides, the harmonic structure almost disappears, and the combined spectrum becomes quasicontinuous (most evidently near the cutoff). At $\varphi = -0.2\pi$, the enhancement in HHG spectrum is maximal and the efficiency of HHG increases by more than three orders, as compared to the spectrum produced by a single fsec- pulse. In this case the conversion efficiency of the highest harmonics (as compared to the fundamental harmonic) is $\sim 10^{-2}$. The plateau region becomes much broader and quasicontinuous (see Fig. 1). This notable feature of the combined spectrum can be used for generating *single* asec pulses. For example, by Fourier converting the frequency components between the 24th and 32nd harmonics back into time domain one can get a *single* pulse with duration ~ 400 asec (see Fig. 2).

For better illustration of the crucial role of the timing effect on the enhancement of HHG, in Fig. 2 we plot the evolution of the time profile of generated pulses at different τ_{del}. All pulses are composed of frequency components between the 24th and 32nd harmonics. As can be seen, all pulses have durations ~ 400–500 asec and have center wavelength ~ 28–30 nm (XUV range). As $\omega_l\tau_{del}$ increases from $-\pi$, the intensity of generated pulses increases and sharply reaches the maximum at $\omega_l\tau_{del} = -0.2\pi$ ($\tau_{del} = -0.1T$). This time instant is in the leading edge of the driving pulse, close to the central peak of fsec pulse. As the controlling pulse moves to the trailing edge of the driving pulse, the intensity of generated pulses gradually decreases. As was mentioned above, at $\varphi = -0.2\pi$ the plateau region of combined HHG is widest. This enables us to use more frequency components for synthesis of *single* pulses and therefore to

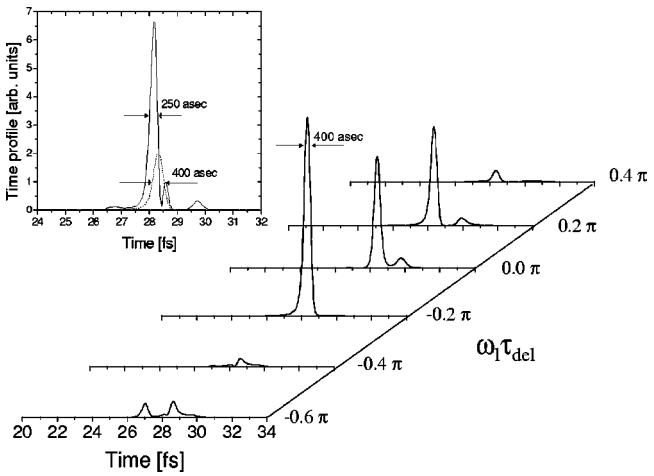

FIG. 2. The time profiles of generated asec pulses at different time delays τ_{del} (pulses are composed from frequency components between the 24th and 32nd harmonics). The inset shows the time profiles of asec pulses obtained by using frequency components between the 20th and 32nd (solid line), and between the 24th and 32nd (dotted line) harmonics. ($\omega_l \tau_{del} = -0.2\pi$.)

achieve much shorter asec pulses. In the inset of Fig. 2 we plot the time profiles of two pulses obtained from the same combined HHG spectrum (shown in Fig. 1). These pulse are obtained by using frequency components between the 24th and 32nd and between the 20th and 32nd harmonics, respectively. In the latter case, the peak intensity of the pulse increases by a factor of 3 and the pulse can be as short as ~ 250 asec.

Besides the enhancement of HHG we also observed the significant enhancement of ionization in combined field of IR fsec and UV asec pulses. In Fig. 3 we plot the time evolution of ionization probability in the combined field of two

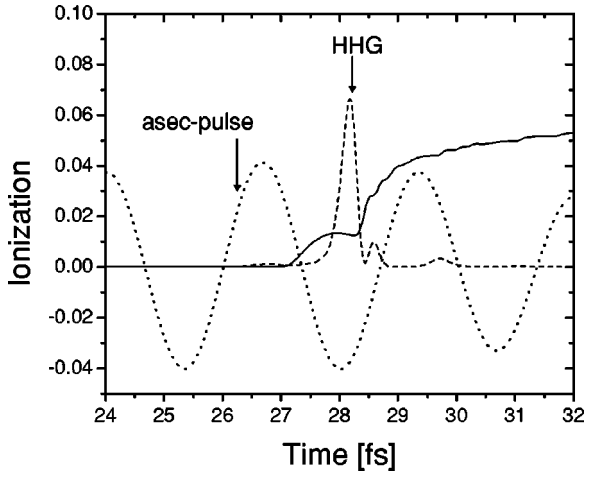

FIG. 3. The ionization probability (solid line), driving field (dotted line), and the profile of a new generated asec pulse (dashed line) on the same time axis. The new generated asec pulse is obtained by using the highest frequency components (between the 24th and 32nd harmonics), its position approximately corresponds to the recombination time t_1 (right arrow). The left arrow indicates the time τ_{del} when the controlling asec pulse is triggered.

laser pulses. For comparison we also plot the normalized electric field of driving pulse and the envelope of the new generated asec pulse on the same time axis. The new asec pulse is generated by using the highest frequency components (between the 24th and 32nd harmonics), therefore its position approximately corresponds to the recombination time t_1 (right arrow). We assume that the controlling asec pulse instantaneously puts electron into the continuum, therefore the time τ_{del} when the controlling asec pulse is triggered can be associated to the birth time t_0 (left arrow). We note that the ionization at the end of the laser pulse $\simeq 5\times 10^{-2}$, which is more than two orders higher than the ones produced by each fsec or asec pulse alone ($\leqslant 10^{-4}$). We assume that the enhancement of ionization and of HHG is due to CREI in H_2^+ ion (see discussions below).

It is worth mentioning the following. The classical model predicts maximum enhancement of HHG when $v_0 = 0$, $\omega_l t_0 = 0.1\pi$, and $\omega_l t_1 = 1.4\pi$ [24], while we observed the maximum enhancement when triggering the controlling asec pulse at $\omega_l \tau_{del} = -0.2\pi$. This discrepancy can easily be solved if we take into account that, in our situation, controlling asec pulse puts an electron into continuum with $v_0 = \omega_{\text{asec}} - E_{ab} \neq 0$ (E_{ab} is the height of the potential barrier at the peak of fsec driving pulse). We have made calculations using the classical model and have found that for the maximal enhancement of HHG at $\varphi = -0.2\pi$ the initial velocity $v_0 \simeq 0.6$. That is in very good agreement with the parameters for fsec and asec pulses used in our quantum calculations. [The classical model also predicts that, independent of v_0, the recombination time always occurs around $\omega_l t_1 = 1.4\pi$.] In principle, for concrete initial conditions, one could find the precise moment for ''turning-on'' the controlling asec pulse to achieve the maximum enhancement of HHG. In our opinion this is the key issue of our new proposed asec controlling technique.

We turn to discuss the applicable range of parameters of pulses for our asec controlling method. *First,* we have made similar simulations for the case where the IR fsec pulse has much higher intensity $I_l = 1.2\times 10^{14}$ W/cm^2 while keeping the parameters of the asec pulse unchanged. In this situation, the ratio between ionization yields produced by single asec, fsec and by combined pulses is 1:10:567 (1.5×10^{-4}, 1.5×10^{-3}, and 8.5×10^{-2}), respectively. The ionization produced by the fsec pulse dominates the ionization from the asec pulse, but it is still 56 times less than the yield produced by *combined* fields. At this intensity, the HHG produced by the fsec pulse alone is also higher as compared to the one shown in Fig. 1. However, we can still observe a significant enhancement in the combined HHG spectra (more than one order) at the same phase $\varphi = -0.2\pi$. The HHG efficiency is still high (2×10^{-3}). The new asec pulse composed of frequency components between 28th and 38th harmonics has a duration ~ 260 asec and has a center wavelength $\sim 23 - 25$ nm. These facts indicate that the observed enhancement of HHG is not due to single fsec or asec pulse alone, but is an effect of *cross correlation* of the two pulses. Our technique works well for the laser intensities $I_l \sim 5\times 10^{13}$–2×10^{14} W/cm^2. In this paper we use relatively low

laser intensity $I_l = 6\times10^{13}$ W/cm^2 in order to reduce backgrounds and to make the *cross correlation* effect more impressive. *Second*, we have gradually increased the duration of the UV pulse. As is expected, the possibility of ''precise control'' gradually ceases and almost disappears when the duration of the ''controlling pulse'' is $\geqslant 0.5T$ ($\sim$1.4 fsec). This value can be considered as an upper limit for the duration of UV pulse to be used in our technique. Behind this limit the combined HHG spectrum remains nearly unchanged when we change the time delay of the controlling pulse as in the case of Fig. 1. Besides, the combined HHG spectrum exhibits clearly harmonic structure with two cutoffs. This is typical signature of a ''two-color'' HHG scheme. The efficiency of HHG in this case is lower as compared to the case of Fig. 1. We assume that the controlling could be efficient when the duration of the UV pulse is around $T/4$ ($\sim$0.65 fsec for the 800-nm driving pulse). *Third*, we have changed the wavelength of the UV pulse. We observe that for $I_l = 6\times10^{13}$ W/cm^2, the HHG enhancement is maximal when the $\lambda_{as} \simeq 115$ nm, i.e., in resonance with the HOMO-LUMO. On both sides of the 115-nm resonance the efficiency of combined HHG decreases. At 70-nm wavelength the efficiency is reduced by a factor $\sim 5-7$. We have made simulations with the aligned model, i.e, H_2^+ with fixed internuclear distance. According to our estimations this is related with the Stark shifted resonances for CREI in H_2^+ [25]. Briefly, the optimum frequency for asec pulse to be used will increase proportionally to the intensity of laser pulse I_l. However, this matter requires thorough analysis and will be discussed in our next investigations.

Last but not least, in this paper we do not consider propagation effects. In principle, our calculations can be justified for the case of low-density gases and short propagation distances (see Ref. [27] for more details). We expect that the enhancement of HHG can be improved by optimizing propagation conditions (i.e., using phase matching), as in the case with HHG in atomic gases [28].

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