Probing nuclear vibration using high-order harmonic generation

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(Received 3 April 2013; published 14 August 2013)

We point out the possibility of probing the nuclear vibration by using the high-order harmonic generation (HHG) with ultrashort laser pulses. By analyzing the HHG spectra obtained from the numerical solution of the time-dependent Schrödinger equation, we find that the intensity of the emitted harmonics is strongly determined not only by the molecular configuration but also by the initial velocity of nuclei. The calculations show that the intensity of HHG is enhanced nearly the time when the internuclear separation takes the equilibrium value and the nuclei are moving closer together. In contrast, with the same initial internuclear separation but with the opposite direction of nuclear velocity, the intensity of emitted light is reduced noticeably. We use that evidence as a tool to probe the nuclear vibration.

DOI: 10.1103/PhysRevA.88.023824 PACS number(s): 42.65.Ky

I. INTRODUCTION

In the last two decades, high-order harmonic generation (HHG) has become one of the most interesting studied topics which attracts much attention due to its promising applications [1,2]. High-order harmonics are emitted when the ionized electron returns and recombines with its parent ion so it is rich in molecular structural information. Itatani *et al*. [3] successfully reproduced the highest occupied molecular orbital (HOMO) of N_2 in the gaseous phase from the experimental HHG data using the ultrashort intense laser with a duration of 30 fs. That achievement is followed by an abundance of works in the direction of dynamic imaging of molecules [4–6]. Scientists are also interested in some results about extracting molecular structural information from the HHG spectra. There is a fitting method proposed in [7,8] for retrieval of the internuclear separation from laser-induced high-order harmonic spectra. With the similar aim of extracting molecular dynamic information, in works [9,10], scientists took advantage of interference effects in the HHG spectra to obtain the internuclear separation in the femtosecond scale. In addition, HHG is an abundant source to probe nuclear dynamics. By analyzing the fine structure of HHG, in [11] authors extracted nuclear vibrational frequency of neutral molecule H_2 and its ion $H_2{}^+$. Baker *et al*. demonstrated a technique that uses HHG to trace the nuclear dynamics and structural rearrangement in a subfemtosecond time scale [12]. Monitoring attosecond (as) dynamics of coherent electron-nuclear wave packets using HHG is also reported in [13] by Bandrauk *et al*.

Recently, the study of HHG taking account of nuclear vibration has carried out by adding the nuclear correlation into the single active electron model [14,15] or numerically solving the time-dependent Schrödinger equation (TDSE) [16,17]. With the later approach, the practically solvable systems hitherto have been limited for those with one or two electrons such as H_2, $H_2{}^+$, $H_3{}^{2+}$ due to the restriction of computer resources. The sensitivity of HHG to vibrational states of molecular ion $H_2{}^+$ and $D_2{}^+$ was reported in [16]. In that work, authors claimed that harmonics emitted from a higher vibrational level are more intense than those from the lower one. In another paper [17], also by numerically solving the TDSE for the neutral molecule H_2 in one-dimensional space, authors showed that nuclear motion would cause considerable changes in the time profile of HHG.

In the direction of studying effects of nuclear vibration on HHG, the preparation of the initial nuclear-electron wave packet, in our point of view, needs to be investigated thoroughly. The initial condition of nuclear should be understood to be as the averaged internuclear separation and the averaged initial nuclear velocity. In the papers [16,17], for instance, the initially total nuclear-electron wave packet contains only one single vibrational state so the effect of nuclear velocity cannot be seen. Lately, by considering the one-dimensional molecule $H_2{}^+$ interacting with the intense laser from the initial wave function whose nuclear motion is described as a superposition of two or three vibrational states, authors pointed out effects of the initial molecular configuration on HHG intensity [18]. However, the influence of the initial velocity of nuclei was not analyzed yet.

In the present work, we study how the initial conditions, say the averaged internuclear separation and the initial nuclear velocity, affect the intensity of high-order harmonic emitted from $H_2{}^+$ and, as a result, will point out the possibility of probing the nuclear dynamics. The two-dimensional (2D) model of $H_2{}^+$ is employed and we will solve numerically the TDSE for obtaining HHG with different initial conditions of the molecule. The initial nuclear wave function is prepared as a superposition of two vibrational states on the electronic lowest system potential curve. The molecule will freely oscillate before the pulsed laser is turned on at time t_{del}, called time delay. By changing the time delay t_{del} when the process of interacting between the molecule and the intense pulsed laser starts, we investigate the dependence of HHG on the time delay t_{del} and hope to see the effects of initial conditions, especially the nuclear velocity, on the intensity of emitted harmonics from which we may use as a tool to probe the nuclear vibration.

The rest of the paper is arranged as follows. In Sec. II we describe the physical model and the method used to calculate the HHG spectra. In Sec. III we show results of calculations and discuss the effects of the initial conditions on the intensity of HHG to point out the possibility of probing nuclear dynamics. Section IV is the conclusion.

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II. THE CALCULATION METHOD

The method of the numerical solution of the TDSE for investigating molecular dynamics can be found in many papers [19–21]. Chelkowski *et al.* [19] uses a one-dimensional (1D) model for $H_2{}^+$ to study dynamics of the electron-nuclear wave packet in the intense laser field. Lappas *et al.* [20] also shows the alignment dependence of HHG from $H_2{}^+$ using the 2D model with fixed nuclei. The 2D model for $H_2{}^+$ is also employed by Takemoto *et al.* [21] to carry out research into the charge-resonance-enhanced ionization. We will call the TDSE method the numerical method of solving the time-dependent Schrödinger equation.

In this paper, we employ the TDSE method for $H_2{}^+$ in a laser field with a single 2D electron and 1D protons using the dipole approximation and the length gauge. The time-dependent Hamiltonian can be written as

$$H(t) = -\frac{1}{2\mu}\frac{\partial^2}{\partial R^2} - \frac{1}{2}\frac{\partial^2}{\partial x^2} - \frac{1}{2}\frac{\partial^2}{\partial y^2} + V_c(x,y,R) + (x\cos\theta + y\sin\theta)E(t), \quad (1)$$

where x, y are electron coordinates with respect to nuclear center of mass; R is the internuclear separation; μ is the reduced mass of two nuclei; θ is called the alignment angle between the laser polarization vector and the molecular axis;

$$V_c(x,y,R) = -\frac{1}{\sqrt{\left(x-\frac{R}{2}\right)^2 + y^2 + a}} - \frac{1}{\sqrt{\left(x+\frac{R}{2}\right)^2 + y^2 + a}} + \frac{1}{R}$$

is a soft-core Coulomb potential. The constant $a = 0.5$ is added to avoid the singularity of the Coulomb potential and mimic the real potential energy curve (PEC) of $H_2{}^+$. The electric field of the laser is $E(t) = E_0 f(t)\sin(\omega t)$ with the sine-square envelope function. Atomic units are used throughout the paper unless stated.

We assume the molecule is prepared in the state as a superposition of single vibrational states which freely oscillate before starting the interaction with the laser field at $t_{\rm del}$. We have the wave function as follows:

$$\Psi(x,y,R,t_{\rm del}) = \sum_v C_v \chi_v(R)\psi(x,y,R)e^{-it_{\rm del}E_v}. \quad (2)$$

Here E_v, χ_v are vibrational eigenvalues and eigenstates of nuclear motion on the lowest PEC of the system. The electronic wave function $\psi(x,y,R)$ is obtained by solving the time-independent Schrödinger equation with each fixed internuclear separation by means of an imaginary time propagation technique [22] using Hamiltonian (1) without the laser-molecule coupling factor. During the process of interacting with the laser field, the total time-dependent wave function is written as follows:

$$\Psi(x,y,R,t_{\rm del},t) = \sum_v C_v \Phi_v(x,y,R,t)e^{-iE_v t_{\rm del}}, \quad (3)$$

where $\Phi_v(x,y,R,t)$ is the time-propagating wave function of the $v^{\rm th}$ state $\chi_v(R)\psi(x,y,R)$ found by solving the TDSE with Hamiltonian (1) using the split operator scheme. In our calculation, a grid of 400 a.u. × 400 a.u is used for electronic motion and the internuclear separation may change from 0.5 a.u. to 10.5 a.u.

We see that the acceleration of the induced dipole moment $\vec{\mathbf{a}}(t_{\rm del},t) = -\vec{\mathbf{E}} - \langle\Psi|\nabla V_c|\Psi\rangle$ depends on $t_{\rm del}$ used as a parameter of the high-order harmonics which are obtained by Fourier transforming of $\vec{\mathbf{a}}(t_{\rm del},t)$ as follows:

$$I(\omega,t_{\rm del}) = \left|\int \vec{\mathbf{a}}(t_{\rm del},t).\vec{\mathbf{n}}\, e^{i\omega t}dt\right|^2, \quad (4)$$

where $\vec{\mathbf{n}}$ is a unit vector on the direction of the polarization vector of the HHG signals.

III. RESULTS AND DISCUSSION

In this part of the paper, we show results calculated with the nuclear initial wave function prepared as a superposition of the two lowest vibrational states, ($v = 0,1$) with the same probabilities. Figure 1 shows the intensity of harmonics released from $H_2{}^+$ aligned parallel to the intense linearly polarized laser varies as a function of time delay $t_{\rm del}$. Here, we plot the intensity of the 21$^{\rm st}$ and 23$^{\rm rd}$ harmonics, the averaged internuclear separation, and the averaged nuclear velocity changing by time delay $t_{\rm del}$. The first thing we see in Fig. 1 is that the intensity of HHG modulates with the same period of nuclear vibration (∼18 fs). This effect can be easily understood because the initial condition changes periodically. With this result, we confirm the results reported in [18] where authors conducted their calculation for 1D $H_2{}^+$. The second but very important point in Fig. 1 we would like to discuss is the correlation between the intensity of harmonics, the internuclear separation and the initial nuclear velocity. In the picture we can see that the HHG intensity reveals maxima nearly the time when the internuclear separation takes the equilibrium value and the nuclei are moving closer together. However, with the same value of the averaged internuclear separation but with the opposite direction of nuclear velocity,

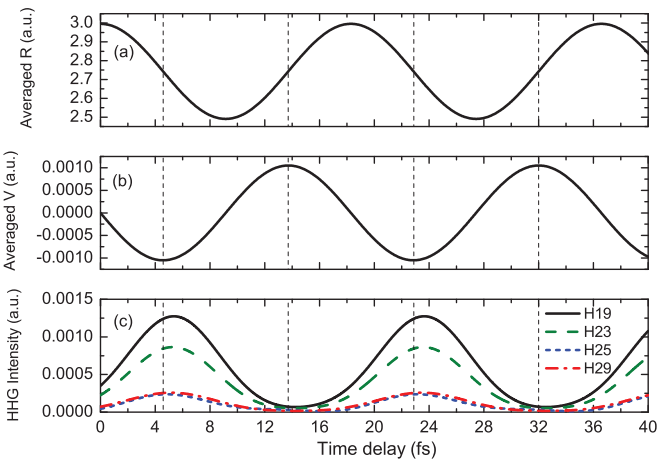

FIG. 1. (Color online) The averaged internuclear separation R (a); the averaged nuclear velocity V (b); and the intensity of 19$^{\rm th}$ (black solid line), 23$^{\rm rd}$ (green dashed line), 25$^{\rm th}$ (blue short-dashed line), and 29$^{\rm th}$ (red dot-dashed line) harmonic as functions of time delay $t_{\rm del}$. A 10-cycle laser pulse with peak intensity of 2.0×10^{14} W cm^{-2} and wavelength of 800 nm is used.

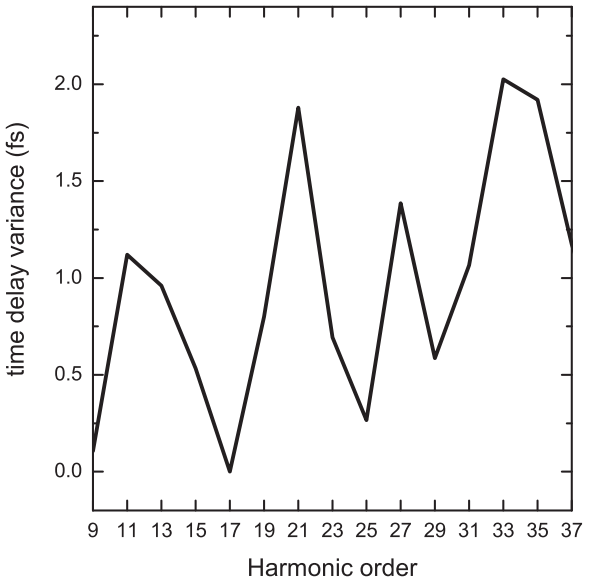

FIG. 2. Time delay variance with harmonics in the plateau region.

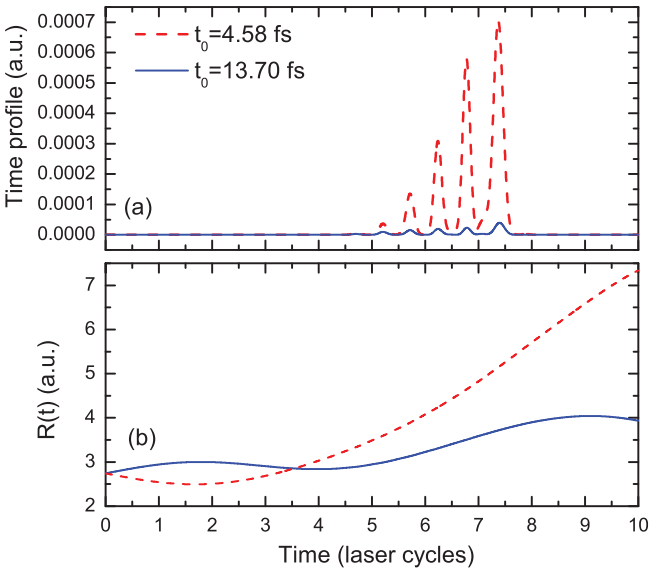

FIG. 3. (Color online) Time profile of 23rd harmonic (a); and the internuclear separation (b) changes as a function of the emitting time with two cases of time delay 4.58 fs (dashed lines) and 13.70 fs (solid lines). The used laser parameters are the same in Fig. 1.

the HHG intensity demonstrates an obvious decrease by around 8 times from the maximum value. In Fig. 1(b), the height of the maxima is in the scale of 10^{-3} which is easily detected by techniques used nowadays. Although Fig. 1 shows the effect only for the 19th, 23rd, 25th, and 29th harmonics, our calculations indicate the similar effect for other harmonic orders in the plateau region whose cutoff is near the 31st. Our results indicate that although maxima position do not absolutely coincide with time when the internuclear separation takes the equilibrium value with each harmonic, the time delay variance is small enough compared to the period of molecular vibration. The time delay variance is defined as the subtraction of the time when the HHG intensity take the maximum value and that when the internuclear separation achieves its equilibrium position. As shown in Fig. 2 the effect occurs for all the orders in the plateau region with some small fluctuations. Thus we can say that relying on the time delay t_{del} dependence of the HHG intensity we can extract the initial information about the internuclear separation and the nuclear velocity at the time when the molecule begins interacting with the intense laser.

Continuously, we check the influence of initial nuclear velocity on the intensity of HHG with the different alignment angles. We analyze the effect for the system with the alignment angle of 90° and for the intensity of harmonics in the plateau region. We do not plot here the figure because it is quite similar to Fig. 1, except only the difference in the intensity. Although the intensity of HHG from perpendicularly aligned molecules is around four times weaker than that with parallel alignment, it also exhibits the properties as mentioned in Fig. 1. It means, once again, the intensity of HHG oscillates with the same period of the nuclear vibration and shows peaks when nuclei are passing through the equilibrium position and nuclear velocity is negative. Therefore we can state that the intensity of HHG is determined by not only the molecular configuration but also the nuclear velocity. Hence, combining with the results of the case of parallel alignment, we can conclude the nuclear

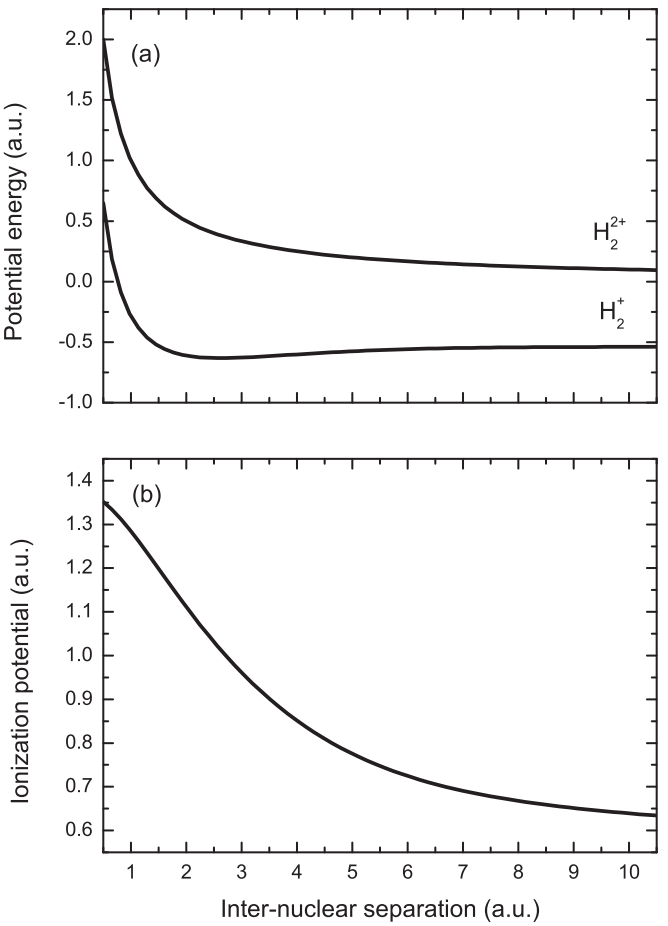

FIG. 4. (a) Potential energy curve of $H_2{}^+$ and $H_2{}^{2+}$; (b) ionization potential of $H_2{}^+$ as a function of the internuclear separation.

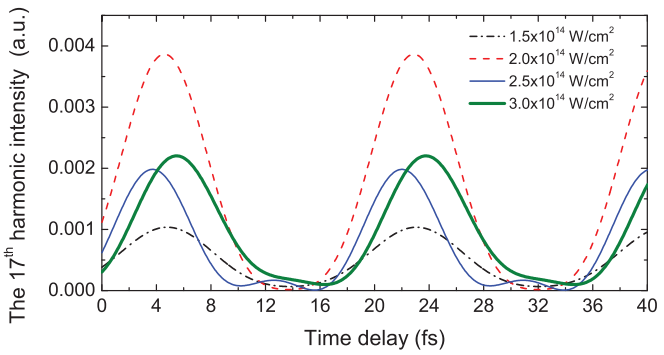

FIG. 5. (Color online) The 17th harmonic intensity changes as a function of time delay with the laser intensity from 1.5×10^{14} W cm^{-2} to 3.0×10^{14} W cm^{-2}.

dynamics can be traced by using the HHG spectra with the ultrashort intense laser pulses.

To have an insight into the relation between the nuclear velocity and the intensity of HHG and to interpret the mentioned above effect, we will do some more investigation. We use the time-frequency analysis technique whose formula is

$$I(\omega, t_{\rm del}; t) = \left| \int \vec{\mathbf{a}}(t_{\rm del}, t') . \vec{\mathbf{n}}\, e^{i\omega t'} e^{(t'-t)^2/2\sigma^2} dt' \right|^2 . \quad (5)$$

The width σ of the window function is chosen as one-tenth of the laser optical period. This analysis technique gives us a time profile of harmonics which depends on orders ω and the emitting time t. The time profiles of the 23rd harmonic order in the case of parallel alignment with two values of time delay (4.58 fs and 13.70 fs) are plotted in Fig. 3(a). We also add the averaged internuclear separations changing from initial values as functions of the emitting time in Fig. 3(b). In Fig. 3(a), one can see that the intensity of 23rd harmonic order changes as a function of the emitting time and depends parametrically on the time delay $t_{\rm del}$. It is obvious that how intense the emitted light is relies strongly on the time when the laser is turned on. This phenomenon may be explained by using the change of the internuclear separation during the interaction time and its relation to the ionization potential. Figure 3(b) shows that, with the same initial value, the internuclear separation can change in two different ways due to the opposite sign of the initial nuclear velocity. At the end of the pulse, the internuclear separation corresponding to time delay 4.58 fs can reach the value of 7 a.u. while it only gets to 4 a.u. if the intense laser is turned on at 13.70 fs. The increase of the internuclear separation will lower the ionization potential of the molecule that makes the electron tunnel easier and leads to the fact that the HHG is more intense. Figure 4 can be a better illustration for the above explanation. Thus, we can conclude that the initial nuclear velocity which creates a taking off of the internuclear separation during the interacting time with the laser pulse may lead to an increase in the HHG intensity.

We continue to change the laser parameters to investigate whether the above-mentioned phenomenon is still observed. When the intensity of the laser pulse changes from 1.5×10^{14} W cm^{-2} to 3.0×10^{14} W cm^{-2} we see that the HHG spectra still reveal the maximum nearly when the averaged internuclear separation takes the equilibrium value as shown in Fig. 5. In other words, with the intensity from 1.5×10^{14} W cm^{-2} to 3.0×10^{14} W cm^{-2} we can say that the laser intensity leads to negligible changes in our results. In addition, we also investigate for lasers with different pulse duration. When the number of cycles varies from 5 to 15, the HHG spectra also show the maximum but their positions are not exactly near the time when the internuclear separation takes the equilibrium value. We see the maximum position oscillates around the equilibrium position of the internuclear separation. In this case, we need to study more the influence of the number of cycles on the HHG spectra. Thus, we can conclude that the nuclear dynamics of $H_2{}^+$ may be probed with appropriate laser parameters.

IV. CONCLUSIONS

In the present paper, we study the effects of the initial condition including the initial averaged internuclear separation and the nuclear velocity, on the intensity of harmonic signal of $H_2{}^+$ to probe the nuclear dynamics. The simulation indicates that not only the molecular configuration but the nuclear velocity also influences noticeably the intensity of HHG. This effect is well checked for two cases, parallel and perpendicular alignment. The simulation also shows that with the same initial internuclear separation, the molecule whose nuclei are passing the equilibrium position and the internuclear separation is decreasing can emit more intense laser light than that from a molecule with the nuclear velocity having the opposite direction. Basing on the nuclear velocity dependence of the HHG intensity, we conclude the nuclear dynamics may be probed.

ACKNOWLEDGMENTS

This project is financially supported by Vietnam's National Foundation for Science and Technology Development (NAFOSTED), Grant No. 103.01-2011.08. We would like to thank Dr. Anh-Thu Le (Kansas State University, USA) for useful discussion.

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