Effects of nuclear vibration on the ionization process of \( H_2^+ \) in ultrashort intense laser field

Ngoc-Loan Phan\(^1\), Tran-Chau Truong\(^2\), Ngoc-Ty Nguyen\(^1\)

\(^1\) Department of Physics, Ho Chi Minh University of Pedagogy, 280 An Duong Vuong Street, District 5, Ho Chi Minh City, Vietnam

\(^2\) Faculty of Foundation Sciences, Ho Chi Minh City University of Technology and Education, 1 Vo Van Ngan Street, Thu Duc District, Ho Chi Minh city, Vietnam

E-mail: tynn@hcmup.edu.vn

Abstract. By numerically solving the time-dependent Schrödinger equation, we calculate the ionization probability of a vibrating \( H_2^+ \) exposed to ultrashort intense laser fields. The results show that the ionization probability increases by time and gets a saturation value. We also find that with some first vibration levels, the ionization probability from a higher vibration level is larger than that from a lower one. However, with higher vibration levels, at a certain level the ionization probability will take maximum and decrease with next levels.

1. Introduction

Since the first optical laser source was invented by Theodore Maiman in 1960 [1], the laser technology has not only grown sharply but also has promoted the scientific and technical revolution. Beside efforts to shorten the pulse duration and to increase the intensity of the laser fields, scientists are especially concerned about the laser-matter interaction. The interaction of ultrashort intense laser pulses with atoms or molecules leads to many nonlinear optical phenomena such as high harmonic generation (HHG) [2–4], above threshold dissociation (ATD), and above threshold ionization (ATI) [5,6].

The ionization process plays an important role in atom, molecule-laser interaction because it is the background to explain above mentioned phenomena. Many works have been conducted to find out ionization mechanisms, specially Keldysh’s article published in 1965 [7]. According to him, there are three mechanisms of ionization of atoms, molecules including tunneling, multiphoton, and above threshold ionization. In fact, which mechanism is dominant depends on frequency, peak intensity of laser fields, and the ionization potential of atoms as well. Unlike atoms, the problems related to interaction between laser and molecules are considerably complex because of a large number of variables. While the problem of intense laser-atom interaction is solved almost completely by using the single active electron approximation (SAE) [2, 4], the scientists continue to study the molecular systems in electromagnetic fields [8–11]. However, due to many degrees of freedom, finding wave functions of molecules and other quantities such as the ionization probability, ionization rate are much more difficult than those for atoms. By using the semi-classical three-step model, the amount of calculation significantly reduces [2]. On the other hand, the numerically solving the time dependent Schrödinger equation (TDSE)
approach can give exact results but requires large computer resource, so now this method is only applied to some simple molecules such as $H_2, H_2^+, H_3^{2+}$.

To simplify the laser-molecule interaction, the nuclei are assumed to be fixed during interaction process and their vibrations are not taken into account when calculating the ionization rate and HHG [3]. However, recently scientists have pointed out many differences between two cases of frozen and moving nuclei in both the HHG spectra and the ionization rate [8–11]. In [8], authors claim that when the initial nuclear vibration is assumed in the ground state, the ionization probabilities and the internuclear distance of molecular ion $H_2^+$ increase in compared with that in the case of fixed nuclei. Ionization rate of $H_2^+$ for different initial vibrational states $\nu = 0 \div 3$ is also studied in [9]. The authors confirm that the faster nuclei vibrate, the higher ionization rate is. Moreover, single and double ionization probabilities of the $H_2^+$ molecule are calculated to explain the changes of the HHG spectra due to influence of nuclear vibration [10]. In [8–10], ionization rate is only calculated with few low vibration states of nuclei, the effects of high nuclear vibration levels to the ionization process have not considered yet. In this article, we calculate the ionization probabilities of $H_2^+$ when two nuclei are prepared in various initial vibrational states $\nu = 0 \div 21$ before the molecule interacts with intense laser fields. In addition, information of nuclear dynamic such as internuclear distance, relative velocity of the two nuclei is also studied to explain ionization related results.

The rest of the paper is arranged as follows. In Sec. 2, we introduce a numerical method to calculate the ionization probability for $H_2^+$. In Sec. 3, we show our results of calculation for the probabilities with fixed and vibrating nuclei. The effects of different vibration levels are also analysed in this section. Sec. 4 is the conclusions.

2. Calculation Method

When a molecular ion $H_2^+$ interacts with a linearly polarized laser field, after being ionized, electron moves along the laser polarization direction. On the other hand, as an electric dipole in an electric field, the molecule is quickly aligned along the polarization vector of the intense laser field. Thus we restrict our study to the one-dimensional model (1D) to reduce the amount of calculations. In this section, we introduce a method to solve the TDSE of a vibrating $H_2^+$ exposed to intense laser fields. After obtaining the time-dependent wave function, we calculate the ionization probabilities and nuclear separation. We use the atomic units ($\hbar = e = m_e = 1$) throughout the paper unless stated. The TDSE of the $H_2^+$ interacting with an intense pulsed laser has the following form

$$i \frac{\partial}{\partial t} \Psi (z, R, t) = \left( - \frac{\partial^2}{2 \partial z^2} - \frac{\partial^2}{2 \mu \partial R^2} + V_C (z, R) + V (z, t) \right) \Psi (z, R, t),$$

where $z$ is the electrons coordinate respect to the center of mass of two nuclei, $R$ is the internuclear distance, $\mu$ is the reduced mass of the two nuclei. $V_C (z, R)$ is the soft Coulomb potential written as

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

The constant $\varepsilon$, called the softening parameter, is added to the Coulomb potential to avoid the singularities. We choose $\varepsilon = 1$ so that the ground state energy in one-dimensional model can mimic the real potential energy curve [6, 11]. With this model, the equilibrium internuclear distance of molecular ion $H_2^+$ is obtained as $R = 2.609 \ a.u.$ The laser-molecule interaction is formulated in length gauge as

$$V (z, t) = z E_0 f (t) \sin (\omega_0 t),$$

where $E_0$ is the laser field amplitude, $f (t)$ is the laser pulse shape, $\omega_0$ is the laser frequency.
where $E_0, \omega_0$ are the electric amplitude and the angular frequency of laser pulse, respectively. $f(t)$, called the envelope of the laser pulse, has a sine-squared shape. The TDSE (1) can be numerically solved by using the split operator method [12]. By that way, the wave function $\Psi(z, R, t)$ is calculated by applying the time evolution operator to the initial wave function $\Psi(z, R, t = 0)$ as follows

$$\Psi(z, R, t) = \exp \left[ -i \int_0^t \hat{H} dt \right] \Psi(z, R, t = 0).$$

(4)

In this study, the approximation BO is utilized in order to calculate the initial wave function. With each nuclear vibration level, characterized by the quantum number $\nu$, the wave function is set as

$$\Psi(z, R, t = 0) = \varphi(z, \bar{R}) \chi_{\nu}(R),$$

(5)

where $\varphi(z, \bar{R}), \chi_{\nu}(R)$ are the electronic and vibration nuclear wave functions, respectively. The electronic wave function $\varphi(z, \bar{R})$ which can be solved by the imaginary relaxation method [13] is first calculated from the Schrödinger equation of electronic system at different values of internuclear $R$ as follows

$$\left(-\frac{\partial^2}{2\partial z^2} + V_C(z, \bar{R})\right) \varphi(z, \bar{R}) = E_e(\bar{R}) \varphi(z, \bar{R}).$$

(6)

The nuclear wave function $\chi_{\nu}(R)$ is also determined by the same method in order to solve the Schrödinger equation of a particle with the reduced mass, bounded in the electronic potential as

$$\left(-\frac{\partial^2}{2\mu \partial R^2} + E_e(R)\right) \chi_{\nu}(R) = E\chi_{\nu}(R).$$

(7)

After obtaining the wave function of the molecule, we continue to calculate the ionization probability. We define the ionization region $S_i$ as

$$S_i = \{z | \text{Abs}(z) > z_i + R/2\},$$

(8)

where $z_i = 20 \text{ a.u.}$ The time-dependent ionization probabilities can be calculated as

$$P_i(t) = \int \int_{S_i} |\Psi(z, R, t)|^2 dzdR.$$  

(9)

Moreover, we also calculate some other quantities, relating to nuclear and electronic dynamics. Concerning the relative dynamics of the nuclei, the internuclear separation is expressed as

$$R(t) = \int \int R|\Psi(z, R, t)|^2 dzdR.$$ 

(10)

Also, the relative velocity between the two nuclei is calculated from the expectation value of the nuclear distance by the following formula $\vartheta(t) = \frac{dR}{dt}$.

In this paper, the numerical grid points are chosen over $0.5 \text{ a.u.} \leq R \leq 20.5 \text{ a.u.}$ and $-800 \text{ a.u.} \leq z \leq 800 \text{ a.u.}$ at interval of $\Delta z = 0.39 \text{ a.u.}$, $\Delta R = 0.04 \text{ a.u.}$ and the time step $\Delta t = 0.18 \text{ a.u.}$
3. Results
In this section, we show our results about effect of molecular vibration on the ionization probabilities. We calculate the time-dependent ionization probabilities of the $H_2^+$ interacting with ultrashort laser pulses in both cases of fixed and moving nuclei at different vibration states. The laser with wave length of 800 nm, pulse duration of 26 fs (10 cycles), peak intensity of $3 \times 10^{14}$ W/cm$^2$, $8 \times 10^{14}$ W/cm$^2$ are used. The results with peak intensity of $3 \times 10^{14}$ W/cm$^2$ are shown in Fig. 1a, which indicate that the onset of ionization occurs after about three optical laser cycles. The ionization probabilities significantly increase in the next cycles, then almost unchanged in the last few ones. In Fig. 1b, the calculation results with peak intensity of $8 \times 10^{14}$ W/cm$^2$ are presented. In Fig. 1, we show that when the laser is turned off, the ionization probabilities rapidly enhance at some first vibration levels, then slightly increase at higher vibration levels. The ionization probability of the $H_2^+$ in the field of laser pulses with peak intensity of $3 \times 10^{14}$ W/cm$^2$, wavelength of 800 nm and pulse duration of 26 fs is quite small (~4.2%) in case of moving nuclei at the ground vibrational state ($v = 0$). However, ionization probabilities strongly increase and equal 22% when nuclei vibrate at $v = 1$; at $v = 2$, they increase to 42% and reach to 51% when $v = 3$ (Fig. 1a). With higher laser intensity, the onset time of ionization sooner occurs and the differences of ionization probabilities (when the laser switch off) between vibration levels are smaller. When the molecule exposed to the laser with intensity of $8 \times 10^{14}$ W/cm$^2$, the ionization probabilities reach to 94% in case of moving nuclei at ground level ($v = 0$), and nearly unchanged when nuclei oscillate at higher vibration states (Figure 1b). The ionization probabilities increase with higher initial vibration levels of nuclei, but they take maximum at a certain level ($v = 9$ for $I = 2 \times 10^{14}$ W/cm$^2$; $v = 11$ for $3 \times 10^{14}$ W/cm$^2$; $v = 15$ for $4 \times 10^{14}$ W/cm$^2$), then decrease with next levels. Those results are obviously illustrated in Fig. 2.

![Figure 1](image-url)  
**Figure 1.** The ionization probabilities of $H_2^+$ in the field of laser pulses with a wavelength of 800 nm, pulse duration of 26 fs, and peak intensities of (a)$3 \times 10^{14}$ W/cm$^2$, (b)$8 \times 10^{14}$ W/cm$^2$ for two cases: fixed (dot line) and moving (solid and dashed lines) nuclei.

Since the internuclear distance is greater with increasing nuclear oscillation of the $H_2^+$, the ionization potential decreases and electron may easily be ionized into the continuum region. To explain the above results of ionization probabilities, the timedependent nuclear separations at various vibration levels of nuclei are also calculated. The results are plotted in Fig. 3. The laser with peaks intensities of $2 \times 10^{14}$ W/cm$^2$ and $4 \times 10^{14}$ W/cm$^2$, wavelength of 800 nm and pulse duration of 26 fs are used. Initially, the higher vibration level of molecular nuclei is, the
Figure 2. The ionization probabilities of $H_2^+$ when lasers switch off. Laser pulses with duration of 26 fs, wavelength of 800 nm, and various intensities are used.

greater internuclear separation is (Fig. 3a). During interaction, the nuclear distances are almost unchanged in the some first laser cycles, then rapidly increase in the next cycles (Fig. 3b). The nuclear separation in case of the initial ground state after the laser is switched off is $R_0 = 3\ a.u.$, and is 13\% greater than its initial value. The difference of internuclear distances when the laser is turned off between vibration level $v = 0$ and $v = 1$ is $\Delta R_{01} = 2.22\ a.u.$; between $v = 1$ and $v = 2$ is $\Delta R_{12} = 1.39\ a.u.$; $\Delta R_{23} = 1.35\ a.u.$; $\Delta R_{34} = 1.01\ a.u.$; $\Delta R_{45} = 0.64\ a.u.$; $\Delta R_{56} = 0.5\ a.u.$; and others. It is obvious that the differences of separations between the lower vibration states are considerable, but gradually reduced and smaller for higher vibration states. This is the reason causing the above conclusion that the ionization probabilities sharply increase with some first vibration levels, slightly increase with next levels, then almost remained unchanged with higher levels.

While molecular ion $H_2^+$ interacts with an ultrashort laser pulse of greater intensity ($4 \times 10^{14}\ W/cm^2$), the internuclear distance rapidly increases even if the nuclei oscillate in ground state ($R_0 = 8.3\ a.u.$) (see in Fig.3a). Therefore, electron is easily ionized, and that leads to a high value of ionization probabilities (31\%). The differences of nuclear separations between various vibration levels are $\Delta R_{01} = 1.35\ a.u.$; $\Delta R_{12} = 1.02\ a.u.$; $\Delta R_{23} = 0.83\ a.u.$; $\Delta R_{34} = 0.73\ a.u.$; etc. These values are smaller than that in the case of the lower intensity laser ($2 \times 10^{14}\ W/cm^2$). Thus, when the molecular ion $H_2^+$ exposed to the laser with higher intensities, the ionization probabilities not only increase more slowly with some first oscillation levels, but also almost is remained with higher vibration levels, compared with the case of lower intensities laser.

The dependences of ionization probabilities on nuclear vibration states may be explained by a combination of the Coulomb potential and the induced-laser potential. In Fig. 4 we plot the total potential energy when the electric field reaches its peak. In the absence of the laser field (bold solid line), the electron is tightly confined in the potential well. Appearance of the laser field leads to the deformation of the potential, and decreases of the potential barrier, thus the tunnel ionization probabilities into continuum region are enhanced. Since the higher nuclear vibration level, the greater internuclear separation, as a consequence the potential well becomes shallower and the ionization rate increases. However, we find from Fig. 1 and Fig. 2 that the ionization probabilities will take maximum at a certain level, then decrease with next levels. This phenomenon can be understood by considering the existence of charge-resonance states of
odd-charge molecular ions in intense laser field. In [6] authors investigated in detail the process of ionization of diatomic ion $H_2^+$ in intense lasers as a function of the internuclear separation, and predicted that ionization rate reaches its maximum at critical nuclear distances. In that sense, the electron population of the excited energy level $1\sigma^+$ is more sufficient than that in ground state $1\sigma^-$, thus the dominance of above-barrier ionization leads to the enhanced ionization. If the internuclear separation is greater than the critical value, the above-barrier ionization of excited level does not occur due to decreasing of inner potential well, that leads to a decrease of ionization probability.

**Figure 3.** The internuclear separation of $H_2^+$ at various initial vibration levels before interacting with laser (Fig. a, solid line) and after turning off the laser (Fig. a, dashed line). Fig. b the time-dependent nuclear separation of $H_2^+$ while interacting with laser with time duration of 26 fs, wavelength of 800 nm, and peak intensity of $2 \times 10^{14}$ W/cm$^2$.

The relative velocities between the two nuclei as a function of laser interaction time are exhibited in Figure 5a. Figure 5b presents the dependences of nuclear velocities on vibration

**Figure 4.** The total potential $V_c(z, R) - zE_0$ for various values of internuclear separations. The corresponding peak intensity of the laser pulse is $2 \times 10^{14}$ W/cm$^2$. 

The relative velocities between the two nuclei as a function of laser interaction time are exhibited in Figure 5a. Figure 5b presents the dependences of nuclear velocities on vibration
levels when the lasers are turned off. We show that when the nuclei oscillate at high vibration states, the relative velocities increase with interaction time. At the low vibration levels, nuclear speeds only increase with some first laser optical cycles, then decrease before the lasers are turned off. Furthermore, in the velocity curves of nuclei, oscillating at low vibration levels, the harmonic properties (appearance of local maximum and minimum) can be seen more clearly. The higher the vibration state is, the more quickly the nuclei move. However, after a certain vibration level, the nuclear relative velocities tend to decrease (Fig. 5b).

![Graph](https://via.placeholder.com/150)

**Figure 5.** The dependences of relative velocities between the two nuclei on (a) interaction time and (b) vibration levels when the laser is turned off. Using laser pulse with time duration of 26 fs, wavelength of 800 nm, and intensity of $3 \times 10^{14} \text{ W/cm}^2$.

4. Conclusions
By numerically solving the TDSE we obtain the ionization probability of a vibrating $H_2^+$ exposed to ultrashort intense laser fields at various vibration levels. The more strongly nuclei oscillate, the more ionization probabilities are. However, with higher vibration levels, the ionization probability will take maximum at a certain level and decrease with next levels. The internuclear separations also increase with increasing vibration states, but more slowly with higher levels. The changes of internuclear separations are the basic to explain the obtained dependences of ionization probabilities on initial nuclear vibration levels.

Acknowledgments
This research is funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number "103.01-2013.37"

References
[1] Maiman T H 1960 Nature **187** 493
[2] Lewenstein M, Balcou Ph, Ivanov M Y, LHuillier A, Corkum P. B. 1994 Phys. Rev. Lett. **49** 2117
[3] Zuo T, Chelkowski S, Bandrauk A D 1993 Phys. Rev. A **48** 3837
[4] Corkum P B 1993 Phys. Rev. Lett. **71** 1994
[5] Bandrauk A D 1993 *Molecules in Laser Fields* (New York: Marcel Dekker)
[6] Zuo T, Bandrauk A D 1995 Phys. Rev. A **52** 2511
[7] Keldysh L V 1965 Sov. Phys. JETP **20** 1307
[8] Qu W X, Chen Z Y, Xu Z Z, Keitel C H 2001 Phys. Rev. A **65** 013402
[9] Guo Y H, He H X, Liu J Y, He G Z 2010 J. Mol. Struc: THEOCHEM **947** 119
[10] Bandrauk A D, Chelkowski S and Lu H 2009 J. Phys. B 42 075602
[11] Do T T H, Nguyen N T. 2013 Journal of Science HCMC UP. 47 184
[12] Feit M D, Fleck J A, and Steiger A 1982 J. Comput. Phys. 47 412
[13] Kosloff R, Tal-Ezer H 1986 Chem. Phys. Lett. 127 223