Ionization of hydrogen molecular ions in an intense laser field via a resonant state

Ying-Jun Jin[a], Xiao-Min Tong[a,b,*], Nobuyuki Toshima[a]

[a]*Institute of Materials Science, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8573, Japan*
[b]*Center for Computational Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 306-8577, Japan*

Abstract

We present a time-dependent Schrödinger equation method in the prolate spheroidal coordinates to study the double ionization of hydrogen molecules in an intense laser field. The time propagation of the electronic wave function is performed by a second order split-operator method in the energy representation. With an adiabatic approximation, we obtain the kinetic energy release (KER) spectra by folding the vibrational wave packet of nuclei with the calculated ionization rates. Our results are in reasonable agreement with the experimental measurement. Furthermore, by including or excluding an individual state in the calculation, we identify that the observed KER peak comes from the ionization of the hydrogen molecular ions via the three-photon resonance of the $2p\sigma_u$ state.

Keywords: Double ionization, Intense laser, Resonant state,

Hydrogen molecules can be doubly ionized by an intense laser field via non-sequential and sequential processes. The non-sequential double ionization of hydrogen molecules was observed experimentally by Niikura *et al.* [1] in the high energy region of the kinetic energy release (KER) spectra. The process was extensively studied by Alnaser *et al.* [2, 3]. If the hydrogen molecules are firstly ionized by the laser and the created molecular ions can be ionized further by the laser independently. In the low energy region, the charge-resonance-enhanced ionization (CREI) predicted by Zuo and Bandrauk [4] for molecular ions was observed in the experiment [5]. The CREI can be classified as a sequential double ionization process. Recently, Litvinyuk *et al.,* [6] observed a high energy peak in the KER spectra when they doubly ionized D_2 molecules using a 480 nm intense laser. The observed peak cannot be explained by the non-sequential double ionization or CREI since the peak position depends on the laser wavelength. They attribute this peak to an enhanced ionization via a three-photon resonance. This could be another type of sequential double ionization of hydrogen molecules in the intense laser field.

To investigate the physical origin of the newly observed peaks, we develop a time-dependent method for the two-center problem. In our model the vibrational wavepackets of hydrogen molecular ions are created through the first ionization of hydrogen molecules and then the ions are ionized by the laser when the vibrational wavepackets move to a large nuclear separation where the electronic ionization potential is small. Within the adiabatic approximation, we separate the electronic motion from the vibration of the nuclei. Let us first focus on the electronic part.

The electronic motion is described by the following time-dependent Schrödinger equation as (atomic units $\hbar = m = e = 1$ are used unless stated otherwise)

$$i\frac{\partial}{\partial t}\Psi(t) = (H_0 + V_{ext}(t))\Psi(t), \tag{1}$$

where H_0 is the Hamiltonian of hydrogen molecular ions and $V_{ext}(t)$ is the interaction of the electron with the laser field. Under the Born-Oppenheimer approximation H_0 is written as

$$H_0 = -\frac{1}{2}\nabla^2 - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{R}. \tag{2}$$

Here r_1 (r_2) is the distance between the electron and nucleus one (two) and R is the internuclear distance. The time-propagation of Eq. (1) is carried out by the second-order-split operator method in the energy representation [7]. For a two-center system naturally we choose the prolate spheroidal coordinates (ξ, η, φ) defined as

$$\xi = \frac{r_1 + r_2}{R} \qquad 1 \le \xi \le \infty \tag{3}$$

$$\eta = \frac{r_1 - r_2}{R} \qquad -1 \le \eta \le 1, \tag{4}$$

and φ the azimuthal angle with respect to the molecular axis. In these coordinates, H_0 is written as

$$H_0 = -\frac{\nabla^2}{2} - \frac{1}{a(\xi + \eta)} - \frac{1}{a(\xi - \eta)} + \frac{1}{R} \quad (5)$$

with $a = R/2$ and

$$\nabla^2 = \frac{1}{a^2(\xi^2 - \eta^2)} \left(\frac{\partial}{\partial \xi}(\xi^2 - 1)\frac{\partial}{\partial \xi} + \right. \quad (6)$$

$$\left. \frac{\partial}{\partial \eta}(1 - \eta^2)\frac{\partial}{\partial \eta} + \frac{\xi^2 - \eta^2}{(\xi^2 - 1)(1 - \eta^2)}\frac{\partial^2}{\partial \varphi^2} \right).$$

Since the Coulomb potentials do not depend on φ, the wave function can be simplified as

$$\psi(\xi, \eta, \varphi) = \Phi^m(\xi, \eta)\frac{e^{im\varphi}}{\sqrt{2\pi}} \quad (7)$$

and the wave function can be reduced to a two-dimensional function. We map ξ and η onto [-1:1] as

$$\xi = 1 + L\frac{1 + x}{1 - x} \quad (8)$$

$$\eta = y, \quad (9)$$

and discretize x, y using a generalized pseudospectral grid [8] with L a mapping parameter used to adjust the grid distribution. The basis functions are

$$f_i(x) = \frac{1}{(1 - x_i^2)P_N'(x_i)}\frac{(1 - x^2)P_N(x)}{x - x_i}, \quad (10)$$

$$f_j(y) = \frac{1}{P_M'(y_i)}\frac{P_M(y)}{y - y_i}. \quad (11)$$

Here $\{x_i\}$ ($\{y_i\}$) are the roots of the N-th (M-th) order Legendre polynomials. We use different basis functions for x and y because the boundary conditions are different for ξ and η. Using the above basis functions, we expand the wave function $\Phi^m(\xi, \eta) \cong \sum_{i,j} C_{i,j}f_i(x)f_j(y)$ and discretize the laser field free Hamiltonian. Diagonalizing the Hamiltonian, we get the eigen energies $\{\epsilon_k\}$ and the eigen wave functions $\{\Phi_k^m(\xi, \eta)\}$. The time-dependent wave function is propagated using the obtained wave functions as a basis set.

Assuming that the laser field is polarized along the molecular axis we write the electron laser interaction as

$$V_{ext}(t) = E_0 a\xi\eta e^{-2\ln 2\, t^2/\tau^2} \cos(\omega t), \quad (12)$$

with E_0 the laser field strength, τ the full width at half magnitude of the laser pulse duration and ω the laser center frequency. The initial electronic state is the ground state $1s\sigma_g$ with $m = 0$. Since m is a good quantum number in the present configuration we drop m hereafter.

To avoid the unphysical reflection of the electronic wave function at the boundary, we add an optical potential [9] to $V_{ext}(t)$ with ξ_c the starting position of the absorber [10]. Using the basis set $\{\Phi_k(\xi, \eta)\}$ obtained above, we propagate the time-dependent wavefunction as

$$C_k(t + \Delta t) = \sum_{k'} e^{-i\epsilon_k \Delta t/2}\langle \Phi_k \mid e^{-iV_{ext}\Delta t} \mid \Phi_{k'} \rangle$$

$$\times e^{-i\epsilon_{k'} \Delta t/2}C_{k'}(t), \quad (13)$$

with $C_k(t) = <\Phi_k|\Psi(t)>$. When the pulse is over, the final ionization probability for a given R is obtained

$$P(R) = 1 - \sum_{\epsilon_k < 0}|C_k(\infty)|^2. \quad (14)$$

Now let us focus on the nuclear vibrational motion. The vibrational ground state $\chi_g(R)$ of the neutral hydrogen molecule is promoted to the vibrational states of hydrogen molecular ion by the laser through the first ionization by a sudden approximation (the Frank-Condon principle). The time-evolution of the vibrational wavepacket satisfies the following Schrödinger equation

$$i\frac{\partial}{\partial t}\chi(R, t) = \left[-\frac{1}{2\mu}\frac{d^2}{dR^2} + V(R) \right]\chi(R, t), \quad (15)$$

with the initial condition $\chi(R, t = t_0) = \chi_g(R)$ and $V(R)$ the adiabatical potential of the ground state of the hydrogen molecular ion. The vibrational wavepacket is propagated in the pseudospectral grid. The $|\chi(R, t - t_0)|^2$ stands for the wave packet density distribution at time t when the molecule is ionized at time t_0. Folding the vibrational wavepacket density with the calculated ionization rates, we obtain the KER spectra as

$$\frac{dP}{dE} = \int_{-\infty}^{\infty} \int_{t_0}^{\infty} \chi^2(R, t - t_0)P(R)W(t_0)|\frac{dR}{dE}|dtdt_0.$$

with $E = 1/R$ and $W(t_0)$ the ionization rate of hydrogen molecules calculated from the molecular tunneling ionization model [11] at time t_0.

Figure 1 shows our simulated KER spectra for 500 nm pulsed laser. When the laser peak intensity is $3 \times 10^{14} W/cm^2$, the main KER peak appears in the high energy area about 8-10 eV, higher than the KER energy of CREI. In our simulation, we have not included the rescattering process so that the peaks are irrelevant to it. This high energy peak in strong laser fields was attributed to the ionization via a three-photon resonant excitation, a new double ionization route which was not observed before. The speculation was based
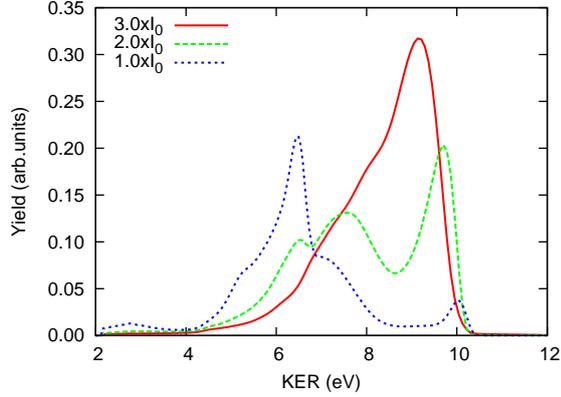
Figure 1: (Color online) The simulated KER spectra due to the double ionization of D_2 in 500 nm pulsed laser fields ($I_0 = 10^{14} W/cm^2$).
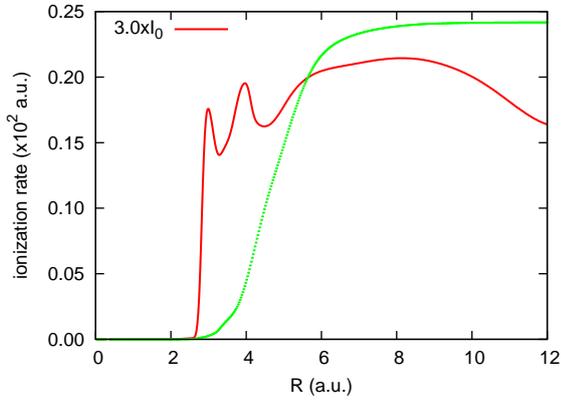
Figure 2: (Color online) The ionization rates of hydrogen molecular ions in a 500 nm pulsed laser field as a function of the internuclear distance. In the simulation, we include (solid) and exclude (dotted line) the $2p\sigma_u$ state.

on that the three-photon energy is in coincidence with the transition energy between the $1s\sigma_g$ and $2p\sigma_u$ at R which corresponds to the KER peak position near 10 eV. For lower laser intensities, namely $2 \times 10^{14} W/cm^2$ and $1 \times 10^{14} W/cm^2$, the high energy KER peaks via three-photon resonant gradually diminish and the main KER peaks appear in the low energy area. Our results are in reasonable agreement with the experimental measurement [6].

To identify the origin of the peaks, we calculate the ionization rate with or without the $2p\sigma_u$ states as shown in Fig. 2. If we remove the $2p\sigma_u$ state artificially in the simulation, the peaks in the small R region disappear completely. The energy difference between the $1s\sigma_g$ and $2p\sigma_u$ states at the peak position (R=2.6 a.u.) coincides with the three-photon energy. The peak around R=4.1 is one-photon resonance and the broad peak around R=9.0 corresponds to CREI. In this way, we confirm that the newly observed peaks are originated from the ionization via the three-photon resonant excitation from $1s\sigma_g$ to $2p\sigma_u$.

References

[1] Niikura, H. et al., Nature **417** (2002) 917.
[2] Alnaser, A. S. et al., Phys. Rev. Lett. **91** (2003) 163002.
[3] Alnaser, A. S. et al., Phys. Rev. Lett. **93** (2004) 183202.
[4] Zuo, T. and Bandrauk, A. D., Phys. Rev. A **52** (1995) R2511.
[5] Gibson, G. N., Li, M., Guo, C., and Neira, J., Phys. Rev. Lett. **79** (1997) 2022.
[6] Litvinyuk, I. V. et al., New J. of Phys. **10** (2008) 083011.
[7] Tong, X. M. and Chu, S. I., Chem. Phys. **217** (1997) 119.
[8] Telnov, D. A. and Chu, S.-I., Phys. Rev. A **59** (1999) 2864.
[9] Perie, J. and Jolicard, G., J. Phys. B **26** (1993) 4491.
[10] Jin, Y.-J., Tong, X.-M., and Toshima, N., Phys. Rev. A **81** (2010) 013408.
[11] Tong, X. M., Zhao, Z. X., and Lin, C. D., Phys. Rev. A **66** (2002) 033402.