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Angular Distributions of Molecular Photofragments by Intense Ultrashort Laser Pulses

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Abstract. We theoretically study the photofragmentation reaction of the hydrogen molecular ion H_2^+ by a single intense ultrashort laser pulse. Simulation results obtained from numerical solutions of time-dependent Schrödinger equations show that quantum interference patterns are constructed in the photofragment spectra and the induced angular distributions of photofragments are sensitive to the wavelength of the laser pulse. These phenomena are successfully explained by using the concept of the light-induced conical intersection.

1. Introduction

Imaging and manipulating chemical reactions of molecules by ultrafast laser pulses has been a longstanding goal of photochemistry and photobiology sciences [1-4]. The pump-probe technique by projecting the initial state onto accessible electronic excited states associated with nuclear motion in the femtosecond (1fs=10^{-15} s) time regime has been developed as an efficient spectroscopy tool [5]. One thus can obtain detailed and substantiated views on the nuclear dynamics in a molecular system, i.e., the dynamics of intramolecular processes and time evolution of the molecular reaction configurations. The essence is to create a coherent wave packet in the molecular system, thus allowing to control quantum coherence and interference phenomena typically by shaping temporal electromagnetic fields. Recent developments of ultrafast laser pulses provide new tools necessary for investigating electron dynamics on its natural attosecond (1 as=10^{-18}s) time scale as compared to the slower nuclear motion on the femtosecond time scale [6,7]. One can now separately study the dynamics of electrons and nuclei and observe pure electronic quantum effects without interference from nuclear motion [8, 9]. Attosecond pulses can induce charge migration across a molecular structure [10, 11], leading to quantum control of chemical reactions on the electron nature time scale [12, 13].

The evolution of the vibration-rotational wave packets in which several vibrational states undergo simultaneously coherent excitation illustrates the intramolecular dynamics of nuclei. Ultrashort laser pulses have provided an access to the coherent excitation of molecular vibrations/rotations. It has been theoretically predicted that the phenomena of the single-pulse-induced quantum interference can be observed in the modulation of angular photodissociation products, providing a direct signature of light-induced conical intersection (LICI) in diatomic molecules [14-16]. Such phenomena have been observed in recent experiments by a transform-limited 30 fs pulse at 795 nm with a peak intensity of 2×10^{13} W/cm^2 into H_2^+ [17]. Most recently, it has been shown that the molecular property of laser-induced quasibound states can be extracted from the transient photofragment momentum distributions, offering a feasible approach to gain an insight into the reaction intermediate directly from photochemical reaction products [18]. These ultrafast phenomena can be understood and analyzed in the framework of light-induced potential (LIP) [1,19-23], which has been commonly used to understand many strong field induced phenomena, including bond softening [24], bond hardening [25], above threshold dissociation (ATD) [26-28], dynamical quenching [29], and stimulated Raman adiabatic passage [30-33].

In the present work we study the molecular photodissociation by a single intense ultrashort laser pulse. Results are obtained from numerical solutions of the time-dependent Schrödinger equation (TDSE) for the benchmark molecular system H_2^+ which has been completely investigated both theoretically and experimentally [34]. It is found that the photofragment angular distributions of molecules are strongly sensitive to the frequency (wavelength) of the driving pulse. Quantum interference patterns are produced at the higher frequency regime. We describe these phenomena by using the

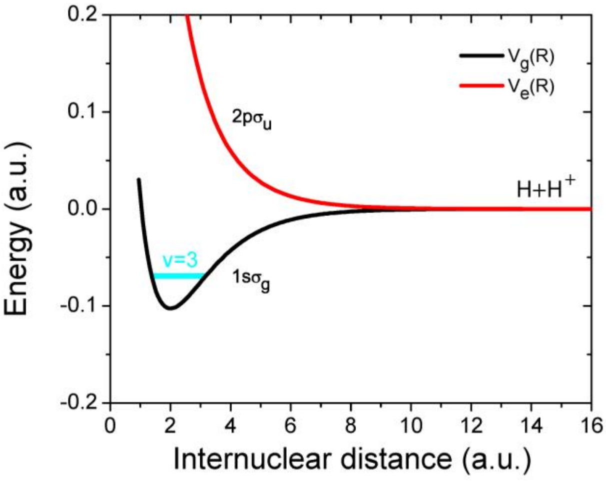

Figure 1: Potential energy curves of H_2^+ as a function of internuclear distance R. The field-free energies of (black line) the ground $1s\sigma_g$ state and (red line) the first excited $2p\sigma_u$ state. v = 3 is the initial vibrational level in the ground $1s\sigma_g$ state.

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concepts of LIPs and the LICI in the adiabatic Floquet representation. Throughout this paper, atomic units (a.u.) are used unless otherwise stated.

2. Numerical Methods

As schematically illustrated in **Figure 1**, the diatomic molecular ion H_2^+ interacts with an intense ultrashort laser pulse *E*(*t*). The potential energy surfaces for the two electronic stats, the $1s\sigma_g$ and the $2p\sigma_u$ states, are taken from Refs. [35,36]. The time evolution of the wave function $\psi(t)$ of molecular ions H_2^+ is computed by solving numerically the TDSE,

$$i\frac{\partial}{\partial t} = H(t)\psi(t) \tag{1}$$

where *H* = *H₀* + *H_L*, is the total Hamiltonian with

$$H_0 = -\frac{1}{2\mathrm{m}}\frac{\partial^2}{\partial^2\mathrm{R}} - \frac{1}{2\mathrm{mR}^2}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) - \frac{1}{2mR^2}\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial^2\phi} + \begin{bmatrix} V_g(R) & 0 \\ 0 & V_e(R) \end{bmatrix} \tag{2}$$

where *m* is the reduced mass of the molecule H_2^+, and *R*, θ and ϕ denote the spherical coordinates of the internuclear vector ***R*** in the laboratory frame. $V_g(R)$ and $V_e(R)$ are the potential energy curves of the $1s\sigma_g$ and $2p\sigma_u$ states, as shown in **Figure 1**. In the present work, a linearly polarized laser field is used to dissociate the molecular ion H_2^+. Due to the cylindrical symmetry of H_0, the motion associated with the azimuthal angle can be separated and *M* is a good quantum number (ΔM = 0). The field-molecule interaction term H_L reads as

$$H_L(R,\theta,t) = -\mu(R)\cos\theta E(t), \tag{3}$$

where μ is the transition dipole momentum and $E(t) = E_0 f(t)\cos\omega t$ is the driving laser field with a Gaussian envelope $f(t) = \exp\left[-4\ln 2(t/\tau)^2\right]$. E_0 is the field amplitude corresponding to maximum intensity $I_0 = c\varepsilon_0 E_0^2/2$ and τ denotes the full width at half maximum (FWHM) of the laser pulse.

The TDSE in Equation (1) is solved numerically by using the split operator method combined with the discrete variable representation (DVR) technique [37, 38]. To avoid reflection of the dissociating wave packet from the end of the grid, an absorption potential G(R) is added at the boundary of the grid. The energy-dependent distribution of the fragments resulting from the ATD can be obtained by calculating the outgoing flux in momentum space [41, 42]. At an asymptotic point R_0 along the internuclear axis, where the field-molecule interaction is negligible and the absorption potential *G(R)* is not switched on, the angle- and time-dependent flux can be expressed as

$$\mathcal{F}(\theta,t)|_{R_0} = \Re\left[-\frac{i}{m}\psi^*(R_0,\theta,t)\frac{\partial\psi(R,\theta,t)}{\partial R}|_{R_0}\right] \tag{4}$$

The discrete Fourier expansion of $\psi(R_0,\theta,t)$ is given by

$$\psi^*(R_0,\theta,t) = \frac{1}{\mathrm{N}}\sum_{\mathrm{n}=1}^{N}\widetilde{\psi}(k_\mathrm{n},\theta,t)\mathrm{e}^{2i\pi(n-1)(n_0-1)} \tag{5}$$

where wave vector $k_n = (2n\pi)/(R_{max} - R_{min})$, and $\widetilde{\psi}(k_n,\theta,t)$ is evaluated by a discrete Fourier transform $\psi(k_n,\theta,t)$. Combining Eqs. (4) and (5) one then obtains,

$$\mathcal{F}(k_n,\theta,t)|_{R_0} = \Re\{\psi^*(R_0,\theta,t)\mathrm{e}^{2i\pi(n-1)(n_0-1)/N} \times \frac{2\pi(n-1)}{m(R_{max}-R_{min})}\widetilde{\psi}(k_\mathrm{n},\theta,t), \tag{6}$$

where R_{max} and R_{min} are the maximum and minimum grid range. $\mathcal{F}(k_\mathrm{n},\theta,t)|_{R_0}$ for $\mathrm{n} \in [1, N/2]$ corresponds to the outgoing flux and the other components is negligible [41,42].

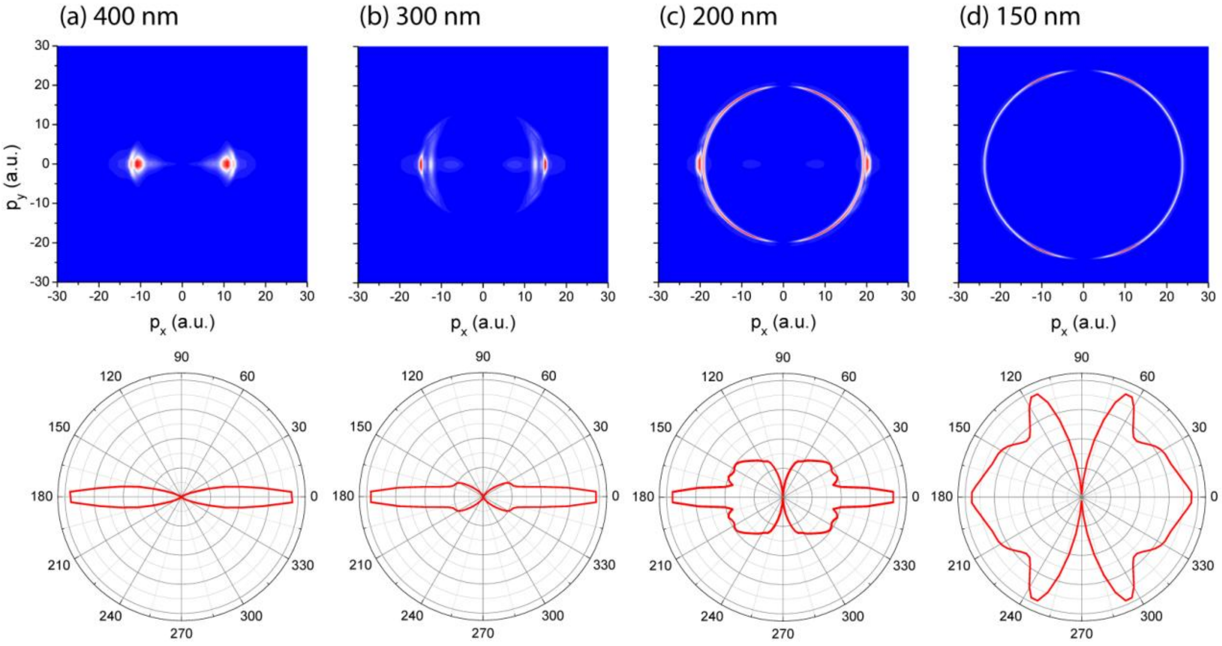

Figure 2: Photofragment momentum and angular distributions of H_2^+ by intense ultrashort laser pulses at wavelengths (a) λ =400 nm (ω = 0.144 a.u.), (b) 300 nm (0.152 a.u.), (c) 200 nm (0.228 a.u.), and (d) 150nm (0.304 a.u.). The pulse intensity $I_0 = 10^{14}\ W/cm^2$ ($E_0 = 5.34 \times 10^{-2} a.u.$) and duration 20 fs FWHM are always fixed. The signal intensities are arbitrary units.