Coherent control of the dissociation probability of H$_2^+$ in $\omega$-3$\omega$ two-color fields

Han Xu,$^1$ Hongtao Hu,$^2$ Xiao-Min Tong,$^3$ Peng Liu,$^{2,4,*}$ Ruxin Li,$^{2,4,*}$ Robert T. Sang,$^1$ and Igor V. Litvinyuk$^1$

$^1$Centre for Quantum Dynamics, Griffith University, Nathan, Queensland 4111, Australia
$^2$State Key Laboratory of High Field Laser Physics, Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800, China
$^3$Center for Computational Sciences and Faculty of Pure and Applied Sciences, University of Tsukuba, Ibaraki 305-8577, Japan
$^4$Collaborative Innovation Center of IFSA (CICIFSA), Shanghai Jiao Tong University, Shanghai 200240, China

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We demonstrate that the coherent control of unimolecular reactions by using a waveform-controlled laser fields can lead to a strong modulation on the yield of the reaction. By using a synthesized $\omega$ (1800-nm) and 3$\omega$ (600-nm) two-color laser field, the probability of photodissociation of H$_2^+$ can be strongly modulated by varying the relative phase between the two colors. The dissociation probability maximizes at different relative phases for protons with different kinetic energy, and such energy dependence can also be qualitatively reproduced by our simulation. We attribute the observed dissociation probability modulation to the interference between two different dissociation pathways which start from the same electronic states and end with the same kinetic energy.

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I. INTRODUCTION

To understand and control the process of laser-matter interaction is one of the ultimate goals of strong-field physics and physical chemistry. In particular, the dissociation of H$_2^+$ in an intense laser field, which is the simplest and most important prototype laser-induced molecular fragmentation process, has been extensively investigated experimentally and theoretically in the last few decades [1]. For example, ultrafast femtosecond laser pulses with controlled time evolution of the electric field has been used to steer the electron motion during the H$_2^+$ dissociation process, where the bound electron can be selectively localized to one of the two protons by waveform-controlled pulses (e.g., carrier-to-envelope-phase (CEP) controlled few-cycle pulses [2–5] and phase-controlled two-color femtosecond pulses) [6], as well as using attosecond EUV pump-femtosecond infrared probe pulses [7,8]. In addition to the control of the electron localization (or equivalently, the asymmetry of proton emission), Hu and Esry have predicted that the probability of the dissociation can also have a CEP dependence [9,10], where the CEP dependence is modulated with a shorter period of $\pi$ than the asymmetry modulation period of 2$\pi$. Here the probability modulation means that the CEP of the driving laser field works as a “switch” for hydrogen dissociation, i.e., the dissociation channel can either be open (with enhanced probability) or closed (with suppressed probability) by controlling the CEP of the laser pulse. The predicted probability control has been examined in CEP-controlled experiments on a H$_2$ target [4] and a H$_2^+$ target [11,12], but the measured probability modulation turns out to be very weak (~5% in Ref. [4], nonvisible in Ref. [11], and ~11% in Ref. [12]), which is much weaker than the asymmetry modulation obtained in the same experiment (~40% in Ref. [4], ~10% in Ref. [11], and ~30% in Ref. [12], correspondingly). And the probability modulation is the result of interference of n− and (n + 2)-photon absorption pathways, while the asymmetry modulation originates from the interference between n− and (n + 1)-photon absorption pathways [10]. Consequently, a much broader frequency bandwidth of the driving few-cycle pulses is required to obtain a probability modulation with similar amplitude as that of asymmetry modulation. As a result, the observed weak probability modulation can be partly explained by the limited spectral bandwidth of the few-cycle driving laser pulse. Ray et al. have investigated the coherent control over dissociative ionization of D$_2$ by using phase-controlled two-color (800-nm and 400-nm) pulses [6], where only a strong phase-dependent asymmetry modulation has been shown, while the phase-dependent dissociation probability controlling has not been addressed.

In order to improve the amplitude of dissociation probability modulation, which is too weak to be practical in the few-cycle pulse case, here we present a $\omega + 3\omega$ two-color control scheme where the hydrogen molecule is dissociatively ionized by a two-color driving pulse which is synthesized from a mid-infrared fundamental pulse (1800 nm) and its third harmonic (600 nm). We show that the strong interference between a one-photon dissociation pathway (H$_2^+$ absorbs one 600 nm photon to dissociate) and a three-photon dissociation pathway (H$_2$ simultaneously absorbs three 1800-nm photons to dissociate) established in two-color fields can lead to a strong modulation (>50%) on the H$_2^+$ dissociation probability, which is approximately 1 order of magnitude higher than the previously reported modulation obtained in a few-cycle scheme.

The physical process of dissociative ionization of H$_2$ in the $\omega + 3\omega$ two-color field can be described by the following simple picture. At the peak of the two-color pulses, the neutral H$_2$ molecule is singly ionized and transits from the ground state of neutral H$_2$ to the ground state (1s$\sigma_g$) of H$_2^+$, followed by the nuclear wave-packet motion due to the different equilibrium internuclear distances between H$_2$ and H$_2^+$. Once the internuclear separation of H$_2^+$ reaches a distance where the energy difference between ground state 1s$\sigma_g$ and first dissociative state 2p$\sigma_u$ equals the energy of a 600-nm photon, the H$_2^+$ can be excited to a dissociative 2p$\sigma_u$ state via bond softening [13] (BS, one 600-nm absorption) or three-photon dissociation [14,15] (3PD, three 1800-nm photon absorption) pathways.
FIG. 1. Experimental setup includes an inline THG setup for generating synthesized 1800-nm and 600-nm two-color fields (see text for detailed descriptions) and COLTRIMS for measuring the momentum of protons. The two-color pulse is sent into COLTRIMS to dissociatively ionize a supersonic hydrogen molecule jet. Potential energy curves of the two lowest lying states of $H_2^+$, as well as the two possible dissociation pathways (three 1800-nm photon absorption and one 600-nm absorption), are shown in the upper-right subfigure.

II. EXPERIMENT

The schematic experimental setup is shown in Fig. 1. The $\omega$-3$\omega$ two-color field is produced in an inline third harmonic generation (THG) setup. The linear-polarized midinfrared fundamental wave (FW, 1800 nm, 60 fs), delivered from a home-built 3-stage optical parametric amplifier (OPA) system [16] pumped by Ti:sapphire crystal (Coherent Elite) is frequency doubled in a type-I $[e(1800 \text{ nm}) + o(1800 \text{ nm}) \rightarrow e(900 \text{ nm})]$ second-harmonic-generation (SHG) beta barium borate (BBO) crystal (thickness = 200 $\mu$m, cut angle = 20.2 deg). Then a type-II $[e(1800 \text{ nm}) + o(900 \text{ nm}) \rightarrow e(600 \text{ nm})]$ sum frequency generation (SFG) BBO crystal (thickness = 400, cut angle = 25.7 deg) is employed to generate the third harmonic pulse. The unnecessary SHG pulse, whose polarization axis is perpendicular to that of FW and THG, is filtered out by a wire grid polarizer. To compensate the group delay between parallel polarized FW and THG pulses, a GD compensator, which includes two polarization rotators (PR) ($\lambda$ at 1800 nm and $\lambda/2$ at 600 nm) and a calcite crystal (thickness 790 $\mu$m, cut angle = 90 deg), is used. The first PR rotates the polarization axis of THG by 90 deg while keeping the axis of the FW pulse unchanged; then the group delay between the cross-polarized FW and THG pulses is compensated after passing through the calcite crystal. Finally the second PR rotates the polarization axis of THG back to be parallel to that of the FW pulse. The relative phase between the FW and THG pulse is controlled by a pair of fused silica wedges installed on a motorized linear stage. The output synthesized two-color field can be expressed as

\[
E(t) = E_\omega \exp \left(-2 \ln 2 \frac{t^2}{\tau_\omega^2}\right) \cos(\omega t) + E_{3\omega} \exp \left(-2 \ln 2 \frac{(t + \Delta t)^2}{\tau_{3\omega}^2}\right) \cos(3\omega t + \Delta \phi),
\]

with $E_\omega, E_{3\omega}$ being the field amplitude, $\tau_\omega$ and $\tau_{3\omega}$ being the pulse duration (FWHM, around 60 fs in our experiment) of FW and THG pulses, respectively, and $\Delta t$ being the group delay between the FW and THG pulses. The relative phase $\Delta \phi$ is controlled by changing the insertion of fused silica wedges from the position where $\Delta t \approx 0$. In the experiment, we scan the relative phase over a range of $6\pi$ with a...
define parameter $P$ as $P(E) = \frac{N(E) - N_{\text{EI}}}{N_{\text{KP}}}$, where $N(E)$ is the KER resolved total proton yield including both up yield ($N_{\text{up}}$), with $p_1 > 0$ and down yield ($N_{\text{down}}$, with $p_1 < 0$), $N_{\text{EI}}$ is the yield averaged over all the phases. As most of the protons are emitted near the polarization axis, we only select those protons with the angle of emission within 30 deg for calculating the $P$ parameter. The measured $P$ as a function of KER and relative phase is shown in Fig. 2(c). Strong periodic phase-dependent modulation of the $P$ parameter in the EI channel and dissociation channels is observed, which can be well fitted by the sine function $P = a \sin(\Delta \phi + c)$, where $a$ is the modulation amplitude and $c$ is the modulation phase. In the EI region with higher KER, the phase of the modulation shows no KER dependence, which gives rise to the straight vertical stripes in the spectrum shown in the upper half of Fig. 2(c). We attribute the $P$ modulation in the EI channel to the variation of peak electric field strength of two-color fields for different $\Delta \phi$, where the EI yield should maximize with the laser peak electric field when $\Delta \phi$ is an integer number of $2\pi$ and so that the two-color fields can add constructively. This simple field strength dependence should be the same for protons with different KER, so the measured modulation in the EI region has no KER dependence. The EI yield modulation can be used for the calibration of the absolute value of $\Delta \phi$, where we set $\Delta \phi$, which corresponds to the maxima of EI yield as integer numbers of $2\pi$. We note that the measured $H_2^+$ yield as a function of $\Delta \phi$ matches the EI yield modulation (not shown here). We also checked the asymmetry of electron localization in the $\omega + 3\omega$ two-color field and found no asymmetry for all $\Delta \phi$ scanned. This is simply due to the fact that the inversion symmetry of the $\omega + 3\omega$ synthesized laser field is not broken, which is different from the $\omega + 2\omega$ experiment [6]. It is interesting to note that the modulation phase shows a significant KER dependence in the lower KER region, and tilted stripes can be observed in the bottom half of Fig. 2(c). We compare the measured $P$ modulation for KER around 0.3 eV and KER around 0.8 eV, as shown in Fig. 3(a), and the difference of the modulation phase is around 45 deg. The significant KER dependence on the modulation phase and modulation amplitude are clearly shown in Figs. 3(b) and 3(c). Such KER dependence cannot be explained by a simple field strength effect. In fact, the KER dependence has been predicted theoretically [10] and has been observed in many experiments addressing CEP-dependent asymmetry modulation [2–5] and yield modulation [4,11,12].

The KER-dependent modulation phase shift is also found in our simulation. We calculate the two-color field-induced dissociative ionization by solving the time-dependent Schrödinger equation which describes the time evolution of the nuclear wave packet (NWP) of $H_2^+$:

$$i \frac{\partial}{\partial t} \begin{pmatrix} \psi_u(R,t) \\ \psi_d(R,t) \end{pmatrix} = \begin{pmatrix} -\frac{1}{2\mu} \frac{d^2}{dR^2} + E_u(R) & -D(R)E(t) \\ -D(R)E(t) & -\frac{1}{2\mu} \frac{d^2}{dR^2} + E_d(R) \end{pmatrix} \begin{pmatrix} \psi_u(R,t) \\ \psi_d(R,t) \end{pmatrix},$$

where $\mu$ is the reduced mass of $H_2$, $R$ the internuclear distance, $D(R)$ the transition dipole between the $\sigma_u$ and $\sigma_d$ states as a function of $R$, and $E(t)$ the time-dependent laser electric field.
The measured red line and blue dashed line are the corresponding sine fitting of and KER of 0.78 eV (blue circle, bin size of 0.04 eV). Solid red line and blue dashed line are the corresponding sine fitting of the measured P modulation, where \( p = a \sin(\Delta \phi + c) \) is used as the fitting function. (b), (c) KER-dependent modulation phase (c parameter) and amplitude (a parameter) with error bars, which is obtained in the sine fitting of the P parameter.

The potential energy curves and transition dipole strengths are calculated in prolate spheroidal coordinates as detailed in Ref. [21]. The peak intensity of FW is set as \( 2 \times 10^{14} \) W/cm\(^2\) and the intensity of the THG pulse as \( 2 \times 10^{13} \) W/cm\(^2\). The initial Frank-Condon NWP is assumed to be launched at each local maximum of the two-color laser field where the ionization rate of the neutral hydrogen molecule peaks and the NWP propagates in the rest of the laser field. The total dissociation yield is calculated by summing yields from each NWP incoherently, since the relative phases between those NWPs are unclear. Figure 2(d) shows the calculated \( P(E) \) parameter for different relative phases. Similar to what we observed in the experiment, the probability modulation shows a strong KER dependence (i.e., tilting stripes) in the KER region of 0–1 eV. The details of the spectrum are different from the experimental measurement, which could possibly come from the assumptions we made for the initial NWP and the omission of the focal volume-averaging effects.

To get a better understanding of the dissociation probability modulation observed in our \( \omega + 3\omega \) experiment, we follow the qualitative approach presented in Ref. [10], writing the kinetic-energy-dependent dissociation probability \( D(E) \) as

\[
D(E) = |\langle u E | F_1 \rangle|^2 + |\langle u E | F_3 \rangle|^2 + 2Re(\langle u E | F_1 \rangle \langle u E | F_3 \rangle^*) \cos \Delta \phi, \tag{4}
\]

where only the interference of the BS dissociation pathway (one 3\( \omega \) photon absorption, transition amplitude of \( e^{i\delta_u} e^{i\Delta \phi} \langle u E | F_1 \rangle \)) and the TPD pathway (three \( \omega \) photon absorption, transition amplitude of \( e^{i\delta_u} \langle u E | F_3 \rangle \)) is taken into consideration, and all the other possible dissociation pathways are neglected to simplify the analysis. \( F_n \) (\( n = 1, 3 \)) is the Floquet representation of the nuclear wave function, \( E \) is KER of the dissociation process, and \( \delta_u \) is the phase shift upon projection to \( \sigma_u (|u E \rangle) \). After expansion, Eq. (3) can be written as

\[
D(E) = |\langle u E | F_1 \rangle|^2 + |\langle u E | F_3 \rangle|^2 + 2Re(\langle u E | F_1 \rangle \langle u E | F_3 \rangle^*) \cos \Delta \phi, \tag{4}
\]

where the first two terms represent the constant background, the third term explains the observed 2\( \pi \)-periodic modulation as a function of \( \Delta \phi \), and the observed KER dependence in the \( P \) spectrum [Figs. 2(c) and 2(d)] should come from the complex transition amplitudes (\( \langle u E | F_n \rangle \)), which contain all the KER dependence. The measured modulation of dissociation probability is around 50%, as shown in Fig. 3(c). However, one cannot attribute the measured modulation completely to the interference effect, since the field strength effect can also modulate the rate of the first ionization (\( H_2 \rightarrow H_2^+ \)), which in turn modulates the dissociation yield. So the modulation is a product of the interference-induced modulation and the field-strength-induced modulation. In spite of this, the interference effect should still dominate, because the measured KER dependence is significant while any field-strength-induced modulation should have no KER dependence.

IV. SUMMARY

To conclude, we show experimentally that the probability of dissociative ionization of \( H_2 \) in a \( \omega + 3\omega \) two-color laser field can be controlled by varying the relative phase between FW and THG pulses, without modulating the asymmetry of the electron localization. In contrast to the previous experiments using a CEP-stabilized few-cycle pulse, a much stronger yield modulation (with period of 2\( \pi \) and amplitude \( \sim 50\% \)) can be achieved. It is interesting to note that the modulation shows significant KER dependence (45-deg shift of the modulation phase over a KER change of 0.5 eV in the low-KER region), and our numerical simulation qualitatively reproduced the observed KER dependence. The clear KER dependence of the probability modulation indicates that the dissociation probability control is mainly a result of quantum interference between different dissociation pathways rather than a simple field strength effect. The presented strong dissociation probability control by tailoring the driving pulse shape is a typical example of coherent control of molecular reaction. Our experiment shows that coherent control can not only alter the product ratios in a laser-induced reaction, which was originally proposed in [22], but also makes it possible to significantly increase the reaction yield along the desired pathway. The probability control, in combination with asymmetry control, will potentially improve overall control of molecular dynamics in a strong laser field.

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