Steering dissociation of Br₂ molecules with two femtosecond pulses via wave packet interference

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The dissociation dynamics of Br₂ molecules induced by two femtosecond pump pulses are studied based on the calculation of time-dependent quantum wave packet. Perpendicular transition from $X^{1}\Sigma_{g}^{+}$ to $A^{3}\Pi_{1u}^{+}$ and ${}^{1}\Pi_{1u}^{+}$ and parallel transition from $X^{1}\Sigma_{g}^{+}$ to $B^{3}\Pi_{0u}^{+}$, involving two product channels Br (${}^{2}P_{3/2}$) +Br (${}^{2}P_{3/2}$) and Br (${}^{2}P_{3/2}$) +Br* (${}^{2}P_{1/2}$), respectively, are taken into account. Two pump pulses create dissociating wave packets interfering with each other. By varying laser parameters, the interference of dissociating wave packets can be controlled, and the dissociation probabilities of Br₂ molecules on the three excited states can be changed to different degrees. The branching ratio of Br*/(Br+Br*) is calculated as a function of pulse delay time and phase difference. © 2008 American Institute of Physics. [DOI: 10.1063/1.2844792]

I. INTRODUCTION

Control of chemical reaction with femtosecond laser pulses has received considerable attention in recent years,^{1–6} such as photoionization,^{7–11} photodissociation,^{12–15} bond softening and hardening,^{16,17} photoassociation,^{18–21} and population transfer.²²⁻²⁵ By measuring the quantum phase of wave packet motion, Ergler et al.⁸ demonstrated that the phase difference between two wave packets corresponding to ionization (D_2^+) and dissociation (D^++D) channels opens a pathway of quantum control. Lagmago Kamta and Bandrauk⁹ studied the influences of the carrier-envelope phase and the molecular orientation on the enhanced excitation and ionization of heteronuclear diatomic molecules. Many approaches of controlling the branching ratio of products have been proposed. Tannor and Rice²⁶ proposed a pump-dump scheme to control selective reaction products. Brumer and Shapiro²⁷ presented a theory used for controlling product ratios in unimolecular reactions by utilizing the coherence of lasers. Amstrup and Henriksen,²⁸ and Elghobashi et al.²⁹ studied how to steer selective bond breaking of HOD molecules based on the IR+UV control scheme. Korolkov and co-workers^{30,31} proposed an approach used to coherently control the ratio of two spin states of matrix isolated molecules, employing two different interfering excitation pathways, i.e., one-photon (UV/visible) versus two-photon (IR +UV/visible) excitations. Marquetand and Engel³² used IR pulses to control the predissociation process of NaI molecules. Recently, Møller et al.³³ and Sarma et al.³⁴ investigated how to control photodissiociation of HOD molecules with UV pulses. By taking the advantages of dynamic Stark shift,^{4,35} the geometric phase,³⁶ the chirped pulses,³⁷ and the carrier-envelope phase,³⁸ one can change the branching ratio

of products in photodissociation to varying degrees. By varying the laser pulse parameters, including the shape, frequency, intensity, phase, and delay time, one can control the branching ratio of products.

In recent years, with the rapid development of the ultrashort and ultrastrong laser pulse technology, the interferences of wave packets, including vibrational nuclear wave packets in bound molecules,^{39–41} bound electronic wave packets in atomic Rydberg states^{42–44} and free electronic wave packets,⁴⁵ have been investigated both theoretically and experimentally. By controlling the interferences of wave packets, one can steer the reconstruction of quantum states, the ionization probability and the alignment of molecular angular momentum and so on. Recently, Stapelfeldt and co-workers^{46,47} studied the interference of dissociating wave packets. They demonstrated that the interference patterns of dissociating wave packets can be determined by laser pulse parameters.

The dissociation probability of molecules is related to the outgoing flux of dissociation channel.⁴⁸ Furthermore, the dissociation dynamics varies with the interference pattern of dissociating wave packets. In the present work, we study how to control the branching ratio by utilizing the interference of dissociating wave packets. The Br₂ molecule is a prototypical system for investigating photodissociation dynamics.^{49–54} Hartke et al.⁵¹ theoretically studied the photodissociation dynamics of Br2 molecules focusing on potential energy curve crossings. Cooper et al.⁵² experimentally studied the photodissociation dynamics of Br₂ molecules at different wavelengths utilizing ion imaging technique. In this paper, we take the Br₂ molecule for example to discuss how to control the branching ratio of dissociation products by the wave packet interference. In Sec. II, we describe the theoretical model. The calculated results are presented and discussed in Sec. III. Finally, the conclusions are briefly summarized in Sec. IV.

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FIG. 1. (Color online) (a) The relevant potential energy curves and transition process of the Br₂ molecule. Two femtosecond laser pulses create dissociating wave packets on each of excited states and open two dissociation channels. (b) The absorption function $G_{abs}(R)$. In the shaded area, $G_{abs}(R) < 1.0$. The parameter R_{abs} determines the central position of absorption region (the shaded area) and the parameter *b* determines how quickly $G_{abs}(R)$ falls to zero.

II. THEORETICAL TREATMENTS

In our theoretical model, four electronic states, the ground state $X \, {}^{1}\Sigma_{g}^{+}$ and the three excited states $A \, {}^{3}\Pi_{1u}^{+}, {}^{1}\Pi_{1u}^{+}$, and $B \, {}^{3}\Pi_{0u}^{+}$, are taken into account, as shown in Fig. 1(a). For convenience, they are abbreviated to *X*, *A*, *C*, and *B*, respectively. Under the action of laser pulses, the Br₂ molecule can be dissociated to two Br atoms in ground state $({}^{2}P_{3/2})$ or to one atom in ground state and the other one in the excited state Br* $({}^{2}P_{1/2})$:

$$\mathrm{Br}_{2} + \hbar\omega \rightarrow \begin{cases} \mathrm{Br}(^{2}P_{3/2}) + \mathrm{Br}(^{2}P_{3/2}) \\ \mathrm{Br}(^{2}P_{3/2}) + \mathrm{Br}^{*}(^{2}P_{1/2}) \end{cases} .$$

Within Born–Oppenheimer approximation, the information of the nuclear dynamics can be obtain by solving the timedependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\mathbf{\Phi} = \hat{H}^0\mathbf{\Phi} \tag{1}$$

with

$$\boldsymbol{\Phi} = \begin{pmatrix} \Phi_X \\ \Phi_B \\ \Phi_A \\ \Phi_C \end{pmatrix}. \tag{2}$$

In the present work, we assume the initial magnetic quantum number M of the Br₂ molecule to be zero. In the linearly polarized laser field, the molecular magnetic quantum number M=0 is conserved, which is equivalent to ignor-

ing the ∂_{φ} term (φ azimuthal angle) in a full threedimensional Hamiltonian.^{11,55,56} The molecular Hamiltonian with an azimuthal symmetry is given by

$$\hat{H}^{0}(R,\theta,t) = \hat{T}_{R}^{0} + \hat{T}_{\theta} + \hat{U}$$

$$= -\frac{\hbar^{2}}{2m} \frac{1}{R} \frac{\partial^{2}}{\partial R^{2}} R - \frac{\hbar^{2}}{2mR^{2}} \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta}\right)$$

$$+ \hat{U}(R,\theta,t), \qquad (3)$$

where *m* is the reduced mass, *R* the internuclear distance, and θ the angle between the laser electric field direction and the molecular axis. In this work, we take *m* as 72 830 a.u. for the Br₂ molecule, which is the average reduced mass of three isotopomers ⁷⁹Br⁷⁹Br, ⁷⁹Br⁸¹Br, and ⁸¹Br⁸¹Br with relative weights of 1:2:1 in natural sample. By setting

$$\begin{pmatrix} \Phi_X \\ \Phi_B \\ \Phi_A \\ \Phi_C \end{pmatrix} = \begin{pmatrix} \Psi_X/R \\ \Psi_B/R \\ \Psi_A/R \\ \Psi_C/R \end{pmatrix},$$
(4)

Eq. (1) can be rewritten as

$$i\hbar\frac{\partial}{\partial t}\Psi = \hat{H}\Psi \tag{5}$$

with

$$\hat{H}(R,\theta,t) = \hat{T}_{R} + \hat{T}_{\theta} + \hat{U}$$

$$= -\frac{\hbar^{2}}{2m}\frac{\partial^{2}}{\partial R^{2}} - \frac{\hbar^{2}}{2mR^{2}}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)$$

$$+ \hat{U}(R,\theta,t), \qquad (6)$$

where

$$\hat{U}(R,\theta,t) = \begin{pmatrix} V_X & W_{XB} & W_{XA} & W_{XC} \\ W_{XB} & V_B & 0 & 0 \\ W_{XA} & 0 & V_A & 0 \\ W_{XC} & 0 & 0 & V_C \end{pmatrix}$$
(7)

with

$$W_{XB} = -\mu_{XB}(R)\varepsilon(t)\cos\theta, \qquad (8)$$

$$W_{XA(C)} = -\mu_{XA(C)}(R)\varepsilon(t)\sin\theta.$$
(9)

In Eq. (7), the diagonal elements represent the potential energy curves of the Br₂ molecule in the absence of laser field. The data of the potential energy curves of the Br₂ molecule are obtained from Refs. 49, 53, and 57. The off-diagonal elements represent the interaction between different electronic states. W_{XB} and $W_{XA(C)}$ differ in their angular dependence because the $B \leftarrow X$ is a parallel transition and yet the $A(C) \leftarrow X$ is a perpendicular transition. The *R*-dependent transition dipole moments $\mu_{Xi}(R)$ (*i*=*A*,*B*,*C*) are given by,^{49,53}

$$\mu_{Xi}(R) = \mu_{0i} + \mu_{1i}(R - 2.3 \text{ Å}), \quad i = A, B, C, \tag{10}$$

where $\mu_{0A}(R)$, $\mu_{0B}(R)$, and $\mu_{0C}(R)$ are equal to 0.1417, 0.385, and 0.498 D, respectively. Moreover, $\mu_{1A}(R)$, $\mu_{1B}(R)$,

and $\mu_{1C}(R)$ are equal to -0.019, 0.29, and -0.31 D/Å in order. The nonadiabatic coupling between excited states is negligible because it is much weaker than the laser-molecule interaction. In the present scheme, two laser pulses are used to dissociate the molecule. The total laser field $\varepsilon(t)$ can be expressed as

$$\varepsilon(t) = \varepsilon_{1}(t) + \varepsilon_{2}(t)$$

= $\varepsilon_{01}f_{1}(t - t_{01})\cos[\omega_{01}(t - t_{01}) + \delta_{1}]$
+ $\varepsilon_{02}f_{2}(t - t_{02})\cos[\omega_{02}(t - t_{02}) + \delta_{2}],$ (11)

where ε_{0k} , t_{0k} , f_k , ω_{0k} , and $\delta_k(k=1,2)$ denote the peak intensity, central time, envelope shape, central frequency, and phase of the *k*th pulse, respectively. The envelope shape of laser pulse f(t) is chosen to be a Gaussian function

$$f(t) = \exp\left[-4\ln 2\left(\frac{t}{T}\right)^2\right],\tag{12}$$

where *T* is the full width at half maximum (FWHM) of laser pulse. The kinetic energy distribution of dissociation products is related to the energy distribution of the laser field (laser spectrum). In the frequency domain, the energy distribution $\tilde{\varepsilon}_{\omega}(\omega)$ is given by

$$\tilde{\varepsilon}_{\omega}(\omega) = \int_{-\infty}^{+\infty} \varepsilon(t) e^{i\omega t} dt = \frac{1}{2} \sum_{k=1,2} e^{i(\omega t_{0k} - \delta_k)} \tilde{f}_k(\omega - \omega_{0k}) \quad (13)$$

with

$$\widetilde{f}(\omega) = \int_{-\infty}^{+\infty} f(t) \cos(\omega t) dt.$$
(14)

The relative velocity v between the two nuclei is related to the photon energy $\hbar \omega$ by energy conservation

$$\frac{1}{2}mv^2 = \hbar\omega + E_0 - E_{d,i}, \quad i = A, B, C,$$
(15)

where E_0 is the energy of the initial wave packet at the ground state X and $E_{d,i}$ is the energy of dissociation limit of the *i*th excited state. Inserting Eq. (15) into Eq. (13), we can obtain the laser spectrum, $\tilde{\varepsilon}_v(v)$, as a function of the relative velocity v.

The initial wave function is chosen to be the rovibrational eigenfunction $|\nu, j\rangle = |0, 0\rangle$ of the ground state *X*. The rovibrational eigenfunction $|\nu, j\rangle$ is a direct product of $P_j(\cos \theta)$ and $\phi_{\nu j}(R)$. $P_j(\cos \theta)$, the Legendre polynomial, is the eigenfunction of the angular kinetic energy operator

$$\hat{T}_{\theta}P_{j}(\cos\theta) = \frac{j(j+1)\hbar^{2}}{2mR^{2}}P_{j}(\cos\theta)$$
(16)

and $\phi_{\nu j}(R)$ is *j*-dependent radial vibrational function. Using Fourier grid Hamiltonian method,⁵⁸ one can compute $\phi_{\nu j}(R)$ by solving numerically the radial Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial R^2} + \frac{j(j+1)\hbar^2}{2mR^2} + V_X(R)\right]\phi_{\nu j}(R) = \epsilon_{\nu j}\phi_{\nu j}(R)$$
(17)

where $\epsilon_{\nu j}$ is the rovibrational energy of the ground state *X*. The time propagation is accomplished by using the split operator method,⁵⁹ that is,

$$\Psi(\tau + \Delta \tau) = e^{-(i/\hbar)\Delta \tau [\hat{T}_R + \hat{T}_{\theta} + \hat{U}(R, \theta, \tau)]} \Psi(\tau)$$

$$\approx e^{-(i/2\hbar)\Delta \tau \hat{T}_R} e^{-(i/2\hbar)\Delta \tau \hat{T}_{\theta}} e^{-(i/\hbar)\Delta \tau \hat{U}(R, \theta, \tau)}$$

$$\times e^{-(i/2\hbar)\Delta \tau \hat{T}_{\theta}} e^{-(i/2\hbar)\Delta \tau \hat{T}_R} \Psi(\tau).$$
(18)

In the momentum space, the operator \hat{T}_R is diagonal, and in the representation of Legendre polynomials, \hat{T}_{θ} is diagonal. Thus, in the calculation, \hat{T}_R is transformed between momentum space and coordinate space by using the fast Fourier transform method,⁶⁰ and \hat{T}_{θ} is switched forward and backward between the polynomial representation and the coordinate space by using discrete variable representation technique.⁶¹ The matrix $\hat{U}(R, \theta, t)$, diagonalized in coordinate space, acts on the wave function directly in coordinate space by multiplication. Meanwhile, in each time step, the wave function is multiplied by an absorption function to avoid the unphysical reflection at the boundary

$$G_{\rm abs}(R) = \{1 + \exp[b(R - R_{\rm abs})]\}^{-1}.$$
 (19)

The parameter R_{abs} determines the central position of absorption region and the parameter *b* determines how quickly $G_{abs}(R)$ falls to zero. The bigger the parameter *b* is, the more quickly $G_{abs}(R)$ falls to zero. So, R_{abs} and *b* should be properly chosen. In the calculation, we set the parameters *b* = 3.0 Å⁻¹ and R_{abs} =37.5 Å with *R* varying from 1.0 to 40.0 Å. The absorption function is shown in Fig. 1(b). $G_{abs}(R)$ equals 1.0 when R < 35.0 Å and falls from 1.0 to 0.0 when *R* varies from 35.0 to 40.0 Å. That is to say, for *R* out of the range [35.0,40.0] Å, the wave functions cannot be changed by the absorption function, although the variable *R* of $G_{abs}(R)$ varies from 1.0 to 40.0 Å.

The branching ratio of dissociation products can be obtained by calculating the outgoing fluxes of different dissociation channels. The outgoing flux of the *i*th channel is defined as

$$F_{i}(t) = \frac{\hbar}{m} \operatorname{Im}\left[\int \Psi_{i}^{*}(R_{0}, \theta, t) \frac{\partial}{\partial R} \Psi_{i}(R, \theta, t)|_{R_{0}} \sin \theta d\theta\right],$$

$$i = A, B, C, \qquad (20)$$

where R_0 is an asymptotic point along the radial axis, which is taken as 6.7 Å in the outside of the damping area [35.0,40.0] Å. So, the results of outgoing fluxes calculated at R_0 are reliable. It should be noted that only the momentum along the dissociation direction (positive momentum) contributes to the outgoing flux and the negative components are negligible. The dissociation probability of the *i*th dissociation channel is calculated by integrating the outgoing flux over the whole propagation time

$$P_i = \int_{-\infty}^{\infty} F_i(t) dt, \quad i = A, B, C.$$
(21)

Finally, the branching ratio of product Br* is given by

$$\Gamma\left(\frac{\mathrm{Br}^*}{\mathrm{Br}+\mathrm{Br}^*}\right) = \frac{P_B}{P_B + P_A + P_C}.$$
(22)

III. RESULTS AND DISCUSSIONS

The transition process and the relevant potential energy curves of the Br_2 molecule are shown in Fig. 1(a). Two femtosecond laser pulses separated in time create two dissociating wave packets on each of the excited states $B^{3}\Pi_{0u}^{+}$, $A^{3}\Pi_{1u}^{+}$, and $^{1}\Pi_{1u}^{+}$. With the time evolution, the two dissociating wave packets overlap and produce an interference structure due to the dispersion. The interference patterns on different excited states are different. By varying the laser parameters, we can control the interference patterns and, therefore, the dissociation probability and the branching ratio. In the calculation, R is required to vary in a 4096-point Fourier grid with the range of [1.0, 40.0] Å. The angular grid points are 60 Gauss-Legendre quadrature points. The central wavelengths of the laser pulses are 420 nm ($\hbar\omega_{01} = \hbar\omega_{02}$ =2.954 eV), the peak intensities $\varepsilon_{01} = \varepsilon_{02} = 5 \times 10^{12} \text{ W/cm}^2$, and the FWHMs $T_1=T_2=2$ fs. Four different sets of laser pulse parameters are shown in Fig. 2. The delay times are 25, 5, 25, and 5 fs in cases I, II, III, and IV in order. Correspondingly, the phase differences are 0, 0, π , and π .

The snapshots of *R*-dependent density functions $|\Psi(R)|^2$ on the three excited states at 10, 300, and 800 fs in case I are shown in Fig. 3. Figures 3(a)-3(c) show the distributions of dissociating wave packets on the excited states $B^{3}\Pi_{0u}^{+}$, $^{1}\Pi_{1u}^{+}$, and $A^{3}\Pi_{1u}^{+}$, respectively. In case I, at t=10 fs, shortly after the excitation, due to the relatively long delay time (Δt =25 fs), the two wave packets on each of the excited states are well separated. At t=300 fs, the interference patterns can be observed and at t=800 fs, the complete interference patterns emerge. We see from Fig. 1(a) that the potential energy curves of $B^{3}\Pi_{0u}^{+}$ and $A^{3}\Pi_{1u}^{+}$ states have wells, while that of ${}^{1}\Pi_{1u}^{+}$ state is a completely repulsive one. Thus, some high vibrational levels of $B^{3}\Pi_{0u}^{+}$ and $A^{3}\Pi_{1u}^{+}$ states can be populated by ultrashort laser pulses with large bandwidth. As a result, the *R*-dependent density functions on $B^{3}\Pi_{0u}^{+}$ and $A {}^{3}\Pi_{1u}^{+}$ states, $|\Psi_{B}(R)|^{2}$ and $|\Psi_{A}(R)|^{2}$, spread in a larger range of internuclear distance at t=800 fs, while $|\Psi_C(R)|^2$ on ${}^{1}\Pi_{1\mu}^+$ state does not. The velocity-dependent density function $|\Psi_{v}(v)|^{2}$ and the laser spectrum $|\tilde{\varepsilon}_{v}(v)|^{2}$ as a function of the relative velocity between the two nuclei are shown in the insets of Fig. 3. The bandwidth of the laser field in the velocity domain ranges from 0 to 40 Å/ps. The v-dependent density function $|\Psi_n(v)|^2$ represents the probability density that the fragment nuclei can be found at the relative velocity v. The relative velocity between the two nuclei is determined by the energy difference between the resonant position and the asymptotic energy of the excited potential energy curve. Due to the different shapes of the excited potential energy curves, the resonant positions of the three excited states are different. Accordingly, the *v*-dependent density functions on the three excited states are also different. As shown in Figs. 3(a)-3(c), four major peaks appear in the distributions of Rand v-dependent density functions. The relative velocities between the two nuclei on $B^{3}\Pi_{0u}^{+}$ and $A^{3}\Pi_{1u}^{+}$ states are in the range from 0 to 20 Å/ps, which lie in the low energy regions of the laser spectra and that on ${}^{1}\Pi_{1u}^{+}$ state ranges from 15 to 25 Å/ps, which lies in the middle region of the laser spectrum.



FIG. 2. (Color online) Four different sets of electric fields $\varepsilon(t)$. The dashed lines show the envelope shapes of laser pulses. The central frequencies, peak intensities, and FWHMs of the two pulses are taken as $\hbar\omega_{01}=\hbar\omega_{02}=2.954 \text{ eV}$ (420 nm), $\varepsilon_{01}=\varepsilon_{02}=5\times10^{12} \text{ W/cm}^2$, and $T_1=T_2=2 \text{ fs}$, respectively.

However, when the delay time is decreased to 5 fs in case II, the interference patterns and dissociation dynamics are obviously changed, as shown in Fig. 4. At t=10 fs, due to the shorter delay time ($\Delta t=5$ fs), the two wave packets are not separated so clearly as those in case I. At t=800 fs, the major interference peaks in the distributions of R- and v-dependent density functions are reduced to two. From the insets, we can see that $|\Psi_v(v)|^2$ varies with the variation of the laser spectrum $|\tilde{\varepsilon}_v(v)|^2$. The interference structure and distribution range of $|\Psi_v(v)|^2$ on each excited state in case II are different from the corresponding ones in case I. In other words, the dissociation dynamics in case II with shorter delay time ($\Delta t=5$ fs) differs from that in case I with longer delay time ($\Delta t=25$ fs).



FIG. 3. (Color online) The *R*-dependent density functions $|\Psi(R)|^2$ on the three excited states at 10, 300, and 800 fs for case I. The velocity-dependent density function $|\Psi_v(v)|^2$ and the laser spectrum $|\tilde{\varepsilon}_v(v)|^2$ as a function of the relative velocity between the two nuclei are shown in the insets.

When the phase difference $\Delta\delta$ between two pump pulses equals π , the *R*-dependent density functions at 10, 300, and 800 fs are shown in Figs. 5 and 6. Figures 5(a)-5(c) show the distributions of dissociating wave packets on $B^{3}\Pi_{0u}^{+}$, ${}^{1}\Pi_{1u}^{+}$, and $A {}^{3}\Pi_{1u}^{+}$ states in case III ($\Delta t = 25$ fs and $\Delta \delta = \pi$), and Figs. 6(a)-6(c) show those in case IV ($\Delta t=5$ fs and $\Delta \delta = \pi$). Comparing Figs. 5 and 6 with Figs. 3 and 4, we find that the effect of phase difference on the dissociation dynamics and the interference patterns in cases II and IV with shorter delay time is larger than that in cases I and III with longer delay time. When $\Delta t = 5$ fs, both the distributions of R- and v-dependent density functions are greatly changed from case II ($\Delta \delta = 0$) to case IV ($\Delta \delta = \pi$). One major peak appears in the distributions of R- and v-dependent density functions in case IV, while two peaks appear in case II. The v-dependent density function on $B^{3}\Pi_{0u}^{+}$ state in case IV ranges in a velocity range from 8 to 20 Å/ps, while that in case II mainly does in a range from 0 to 15 Å/ps. At v ≈ 20 Å/ps, the *v*-dependent density function on ${}^{1}\Pi_{1u}^{+}$ state displays a peak in case IV but a trough in case II. Also, the v-dependent density function on $A^{3}\Pi_{1u}^{+}$ state in case IV ranges in a region from 0 to 15 Å/ps, while that in case II ranges from 10 to 20 Å/ps. However, the changes of the distributions of R- and v-dependent density functions from case I to case III are not so obvious as those from case II to case



FIG. 4. (Color online) The *R*-dependent density functions $|\Psi(R)|^2$ on the three excited states at 10, 300, and 800 fs for case II. The velocity-dependent density function $|\Psi_v(v)|^2$ and the laser spectrum $|\tilde{\varepsilon}_v(v)|^2$ as a function of the relative velocity between the two nuclei are shown in the insets.

IV. That is to say, in cases II and IV with shorter delay time, the dissociation dynamics can be obviously affected by the phase difference, but in cases I and III with longer delay time, the phase difference has a little effect on the dissociation dynamics.

The v- and θ -dependent density distributions of Br fragments, $|\Psi(v,\theta)|^2$, are shown in Fig. 7, where panels (a)–(d) show the distributions in cases I-IV in order. In each panel, the arrow indicates the direction of the laser polarization vector. The inner rings correspond to the products Br+Br*, which result from the parallel transition $B^{3}\Pi_{0u}^{+} \leftarrow X^{1}\Sigma_{e}^{+}$, while the outer ones correspond to the products Br+Br, which result from the perpendicular transition ${}^{1}\Pi_{1u}^{+}(A {}^{3}\Pi_{1u}^{+})$ $\leftarrow X^{1}\Sigma_{g}^{+}$. The interference pattern can also be seen from Fig. 7. We find that the interference patterns and the densities of the distributions are different for different delay times and phase differences. For the longer delay time (25 fs), a little change can be found from panels (a) and (c). While changes from panels (b) and (d) are obvious for the shorter delay time (5 fs). The outer rings have two interference peaks in panel (b), but only one peak appears in the outer rings in panel (d). Meanwhile, the density of outer rings in panel (d) is much larger than that in panel (b). The inner rings in panels (b) and (d) are obviously different in the shape and density of the



FIG. 5. (Color online) The *R*-dependent density functions $|\Psi(R)|^2$ on the three excited states at 10, 300, and 800 fs for case III. The velocity-dependent density function $|\Psi_v(v)|^2$ and the laser spectrum $|\tilde{\varepsilon}_v(v)|^2$ as a function of the relative velocity between the two nuclei are shown in the insets.

distribution. In short, from v- and θ -dependent density distribution of Br fragments, we can conclude that both the delay time and the phase difference have important effects on the dissociation dynamics and the final dissociation products.

The time-dependent dissociation probabilities of the Br₂ molecule on the three excited states, defined as $P_i(t) = \int_{-\infty}^{t} F_i(\tau) d\tau$, $i=B \, {}^{3}\Pi_{0u}^{+}$, ${}^{1}\Pi_{1u}^{+}$, and $A \, {}^{3}\Pi_{1u}^{+}$, are shown in Fig. 8 for the above four cases. Panel (a) shows the dissociation probabilities at $\Delta t=25$ fs (cases I and III), and panel (b) shows those at $\Delta t=5$ fs (cases II and IV). When the propagation time is longer than 1000 fs, the value of $P_i(t)$ is convergent and hence is the final dissociation probability defined by Eq. (21). In each case, different dissociation probabilities correspond to different wave packet interference patterns.

When the phase difference between two laser pulses is fixed, the dissociation probability and the branching ratio vary according to the delay time between two laser pulses. From Fig. 8, we can see that when $\Delta\delta=0$, the dissociation probability of the Br₂ molecule on ${}^{1}\Pi_{1u}^{+}$ state is 0.027 at Δt =25 fs in case I, and 0.0089 at $\Delta t=5$ fs in case II. The dissociation probabilities on the other two states in case II are similar to those in case I. Thus, the branching ratio $\Gamma(Br^*/Br+Br^*)$ in case II is larger than that in case I. However, when $\Delta\delta=\pi$, the dissociation probability on ${}^{1}\Pi_{1u}^{+}$ state



FIG. 6. (Color online) The *R*-dependent density functions $|\Psi(R)|^2$ on the three excited states at 10, 300, and 800 fs for case IV. The velocity-dependent density function $|\Psi_v(v)|^2$ and the laser spectrum $|\tilde{\varepsilon}_v(v)|^2$ as a function of the relative velocity between the two nuclei are shown in the insets.

is 0.027 at Δt =25 fs in case III, and 0.044 at Δt =5 fs in case IV. Meanwhile, the dissociation probability on $B^{3}\Pi_{0u}^{+}$ ($A^{3}\Pi_{1u}^{+}$) state is 0.0064 (0.000 79) in case III, and 0.0061 (0.0012) in case IV. Thus, the branching ratio in case IV is less than that in case III.

The effect of phase difference on the dissociation probability is related to delay time. For a longer delay time, for example, $\Delta t = 25$ fs, the phase difference has no obvious effect on the probability, as shown in Fig. 8(a). The dissociation probability on ${}^{1}\Pi_{1u}^{+}$ state at $\Delta \delta = 0$ (case I) is almost the same as that at $\Delta \delta = \pi$ (case III) and the dissociation probability on A ${}^{3}\Pi_{1u}^{+}$ state in case I is nearly the same as that in case III. There is a minor difference between the dissociation probabilities on $B^{3}\Pi_{0u}^{+}$ state in cases I and III. Thus, the branching ratios in cases I and III are almost the same. However, for a shorter delay time, $\Delta t = 5$ fs, the phase difference has obvious effect on the dissociation probability, as shown in Fig. 8(b). When the phase difference changes from 0 (case II) to π (case IV), the dissociation probabilities on ${}^{1}\Pi_{1u}^{+}$ state and $A^{3}\Pi_{1u}^{+}$ state increase while that on $B^{3}\Pi_{0u}^{+}$ state decreases. As a result, the branching ratio $\Gamma(Br^*/Br+Br^*)$ in case IV is less than that in case II. It is because the phase difference has a little effect on the dissociation dynamics in cases I and III with longer delay time that the corresponding



FIG. 7. The v- and θ -dependent density distributions $|\Psi(v, \theta)|^2$ of Br fragments. The (v, θ) are taken as the grid points in polar coordinates. Panels (a)–(d) show the distributions in cases I–IV in order. The arrow indicates the direction of the laser polarization vector. v_{\parallel} and v_{\perp} denote velocity components parallel with and perpendicular to the laser polarization vector, respectively.

dissociation probabilities in the two cases are nearly the same. However, in cases II and IV with shorter delay time, the dissociation probability and the branching ratio vary with phase difference obviously.

In Fig. 9, we show the branching ratio $\Gamma(Br^*/Br+Br^*)$ as a function of delay time and phase difference. From Figs. 9(a) and 9(b), we can see that the branching ratio is not a monotonic function of the two parameters (phase difference and delay time) but fluctuates with the variation of the two parameters. The variation of branching ratio with phase difference is not obvious until the delay time is shorter than 10 fs. In Fig. 9(c), when the delay time $\Delta t=25$ fs, the



FIG. 8. (Color online) The time-dependent dissociation probabilities on the three excited states in the four cases. (a) The lines without and with symbols represent the dissociation probabilities in case I (Δt =25 fs, $\Delta \delta$ =0) and case III (Δt =25 fs, $\Delta \delta$ = π), respectively. (b) The lines without and with symbols represent the dissociation probabilities in case II (Δt =5 fs, $\Delta \delta$ =0) and case IV (Δt =5 fs, $\Delta \delta$ = π), respectively.

branching ratio equals approximately a constant (about 0.19). However, when Δt =6.5, 6.0, and 5.5 fs, the corresponding branching ratios vary obviously (from 0.1 to 0.4) with phase difference. It should be noted that for different delay times, the branching ratios peak at different values of phase difference. In Fig. 9(d), the branching ratios as a function of delay time are shown at $\Delta \delta$ =0 and π . It can be seen that the branching ratio fluctuates with delay time, and the fluctuation becomes stronger when delay time decreases. The peaks of the branching ratio at $\Delta \delta$ = π correspond to the troughs of the branching ratio at $\Delta \delta$ =0. In short, both the phase difference and the delay time between the two laser pulses have important effects on the branching ratio of the products.

IV. CONCLUSIONS

In this paper, we have studied the dissociation probability and branching ratio for the Br2 molecule in femtosecond laser field. The ground state $X^{1}\Sigma_{g}^{+}$ and three dissociation excited states $B^{3}\Pi_{0u}^{+}$, $A^{3}\Pi_{1u}^{+}$, and ${}^{s_{1}}\Pi_{1u}^{+}$ are taken into account in our calculations. Two pump pulses create dissociating wave packets interfering with each other. Varying the laser parameters, we can control the interference of dissociating wave packets and hence steer the branching ratio of dissociation products. We have depicted the interference patterns of dissociating wave packets and calculated the dissociation probabilities of the Br2 molecule in the three excited states for four different sets of laser parameters. Comparing the results of the four cases, we find that the phase difference and the delay time between the two pulses have effects on the dissociation probabilities of the products on the three excited states, especially on the ${}^{1}\Pi_{1u}^{+}$ state. The branching ratio has also been calculated as a function of delay time and



FIG. 9. (Color) The branching ratio $\Gamma(Br^*/Br+Br^*)$ as a function of delay time and phase difference. (a) The branching ratio vs delay time and phase difference [three-dimensional (3D) plot]. (b) The branching ratio vs delay time and phase difference [(2D) plot]. (c) The branching ratio vs phase difference for four fixed delay times. (d) The branching ratio vs delay time for two fixed phase differences.

phase difference. The wave packet interference and the branching ratio strongly depend on the phase difference for a relatively short delay time. The branching ratio of the products can be controlled by choosing proper phase difference and delay time between the two laser pulses. The method proposed in this paper may be applied to the other molecular systems.

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