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Coherent Control of Photofragment Separation in the Dissociative Ionization of IBr

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We have investigated coherent control of the dissociative ionization of IBr using phase-controlled two-color $\omega + 2\omega$ laser pulses with an intensity of 1.0×10^{12} W/cm and a pulse duration of 130 fs. The directional asymmetries of the photofragment angular distributions showed oscillation behavior dependent on the relative phase difference between the ω and 2ω pulses. The phase dependencies of the directional asymmetries observed for iodine ions and bromine ions were out of phase with each other. This result shows that a phase-controlled $\omega + 2\omega$ optical field can produce molecular orientation in which the optical field discriminates between parallel and antiparallel configuration of molecules that have a permanent dipole.

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Coherent control of chemical reactivity by lasers has the potential to provide the means for complete reaction control [1,2]. There are two approaches to coherent control: a time-domain approach and a frequency-domain approach. The time-domain approach involves the manipulation of the molecular reaction dynamics in the real-time domain before rapid internal energy redistribution occurs [3]. Recent experiments have used feedback optimization of shaped femtosecond laser pulses for complete control of wave packet dynamics [4–6].

The frequency-domain approach involves the manipulation of the interference between two or more optical transitions. This approach can be understood in terms of an analogy with Young's double-slit experiment, in which constructive of destructive interference promotes or suppresses the target reaction path. Shapiro *et al.* have proposed a strategy that uses the interference between a dipole-allowed three-photon transition induced by fundamental frequency light and a one-photon transition induced by third-harmonic light (the $\omega + 3\omega$ scheme) [7]. The $\omega + 3\omega$ scheme has been used to ionize atoms, diatomic molecules, and polyatomic molecules [8]. Zhu *et al.* have achieved reaction control of the branching ratio between photoionization and photodissociation of HI molecules [9].

The uses of the interference between a one-photon transition induced by second-harmonic light and a two-photon transition induced by fundamental light (the $\omega + 2\omega$ scheme) have also been investigated [10–17]. In this scheme, because the final state differ in parity owing to the different selection rules of the one- and two-photon transitions, the interference between the two transitions can be observed in the photofragment angular distribution as the directional asymmetries [11]. This type of interference has been observed in photoelectrons in the ionization of atoms [12], in photocurrents in semiconductors [13], and in above-threshold ionization [14]. Charron *et al.* have suggested the application of the $\omega + 2\omega$ scheme to the photodissociation of HD^+ molecules, and the scheme can also be used for directional separation of photofragments [15]. Experimental attempts to control molecular photodissociation using an $\omega + 2\omega$ scheme have been reported for HD^+ [16] and ${H_2}^+$ [17] molecules. Strong directional asymmetries of the positively charged nuclear fragments and photoelectrons have been observed in both experiments; two significant results were observed. The first result was the phase-dependent behavior of the photoelectrons; they were preferentially emitted in the direction as the maximum of asymmetric electric field, a result that seems counterintuitive [16,17]. This anomaly has been explained by taking into account the Coulombic attraction of the parent ion in the exact non-Born-Oppenheimer numerical solution of the time-dependent Schrödinger equation [18]. The second result is the phase-dependent behavior of the H^+ and D^+ nuclear fragments; both were preferentially emitted in the same direction [16]. Charron *et al.* have explained this result as a case in which there is a high-frequency region where the effect of the permanent dipole is invalid [15]. So far, to our knowledge, no one has observed directional separation of photofragments using the $\omega + 2\omega$ scheme. In this Letter, we report on our investigation of coherent control of the dissociative ionization of IBr using the $\omega + 2\omega$ scheme with intense (1.0×10^{12} W/cm), ultrashort (130 fs), and two-color (800 and 400 nm) laser pulses. We performed one-dimensional photofragment translational spectroscopy. The directional asymmetries in the fragment-emission patterns showed strong phase dependence: the directional asymmetries of the iodine and bromine ions were out of phase with each other. We will discuss our results from the viewpoint of the molecular orientation in which the phase-controlled laser fields discriminate between parallel and antiparallel configurations of polar molecules.

The experimental apparatus, which has been described elsewhere [19], consisted of a Ti:sapphire laser system, a

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Mach-Zehnder interferometer, and an ion time-of-flight (TOF) mass spectrometer. Briefly, laser pulses of 400 and 800 nm (the fundamental and the second-harmonic), 130 fs duration, and 20 Hz repetition rate were focused on the molecular supersonic beam in the reaction chamber using a spherical mirror with a radius of 250 mm, giving peak intensities of up to 10^{14} W/cm^2. The polarizations of the ω and 2ω pulses were both parallel to the detection axis. The total electric field of the linearly polarized optical fields of the two frequencies, the fundamental (ω) and its second-harmonic (2ω), is given by $E(t) = E_1 \cos(\omega t) + E_2 \cos(2\omega t + \phi)$, where E_1 and E_2 are the amplitudes of the electric fields and ϕ is the relative phase difference between the fundamental and the second-harmonic. The relative phase difference between the ω and 2ω pulses was scanned by rotating the quartz plate (3 mm thickness) inserted in the path of the 2ω beam in the Mach-Zehnder interferometer. The relative phase difference between the ω and 2ω pulses was determined from the incident angle and the refractive index of the quartz plate at 400 nm ($n = 1.470$). To calibrate the relative phase difference between the two beams, we measured the interference between the first 2ω beam and the second 2ω beam produced by a second frequency-doubling crystal in the reaction chamber [14]. A gas sample consisting of IBr diluted with helium was introduced via a supersonic beam source. After ionization by the laser pulse, ions traveled across the 200-mm-long drift tube and were detected by a microchannel plate. TOF spectra were recorded using a digital oscilloscope by taking the average of 512 measurements. We minimized the contributions from higher clusters by choosing only the initial part of the molecular beam pulse.

Dissociative ionization of molecules in intense laser fields has been thoroughly investigated [20–22]. The TOF spectrum of the singly charged ions produced by dissociative ionization of IBr with the 800-nm pulse alone shows singly charged Br^+, I^+, and parent IBr^+ ions [Fig. 1(a)]. The IBr^+ ions show a double peak due to the bromine isotopes ($I^{79}Br$ and $I^{81}Br$). Each photofragment shows a pair of peaks, one resulting from ions that flew directly toward the detector, the other from ions that flew in the backward direction before being reversed by the extraction fields. The spacing of the forward and backward peaks reflects the kinetic energy release.

To calibrate the kinetic energy of the photofragments, we measured the neutral spin-orbit excited state of iodine atoms $I^*(^2P_{1/2})$ and bromine atoms $Br^*(^2P_{1/2})$ produced by one-photon dissociation with a nanosecond laser: $\lambda = 280.69$ nm for $I^*(^2P_{1/2})$; $\lambda = 277.74$ nm for $Br^*(^2P_{1/2})$ [Fig. 1(b)]. Each neutral atom was ionized by the same laser via two-photon resonance enhanced multiphoton ionization (REMPI). One-photon dissociation yields iodine atoms with a kinetic energy of 0.64 eV (987 m/s) and bromine atoms with a kinetic energy of 1.34 eV (1802 m/s) [23]. By calibrating the spectrometer using the results from the nanosecond laser, we determined the kinetic energy of the photofragments: 0.63 eV (980 m/s) for the I^+ ions and 0.93 eV (1500 m/s) for the Br^+ ions. We assigned each ion as being produced via the $IBr^+ \rightarrow I^+ + Br$ channel or the $IBr^+ \rightarrow I + Br^+$ channel, respectively, as for I_2 and Br_2 [22]. Excitation at intensities greater than 10^{13} W/cm^2 induced a Coulomb explosion pattern that accompanied the $IBr^{+(p+q)} \rightarrow I^{+p} + Br^{+q}$ channels (not shown here).

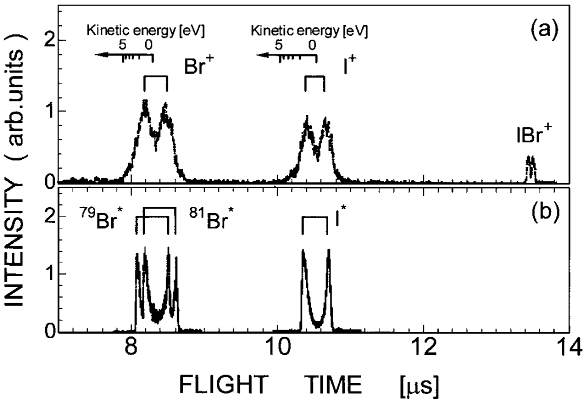

FIG. 1. (a) TOF spectra of Br^+, I^+, and IBr^+ produced by the dissociative ionization of IBr molecules at 800 nm. The scales in the figure have the kinetic energy of the photofragments calibrated by means of nanosecond-pulse excitation. (b) The TOF spectrum of spin-orbit excited iodine and bromine atoms produced by one-photon dissociation of IBr molecules at 280 nm for the calibration of kinetic energy under the conditions used in the experiment with femtosecond-pulse excitation.

When IBr molecules were irradiated with both the fundamental and the second-harmonic beams with zero time delay, directional asymmetries in the photofragment angular distributions were clearly observed in the TOF spectrum. The intensity of the forward peak in the I^+ signal was larger than that of the backward peak [Fig. 2(a)]. This asymmetry shows that the I^+ ions were preferentially emitted toward the detector at $\phi = 0$, when the electric field maximum pointed toward the detector. By contrast, the Br^+ ions were emitted preferentially away from the detector. Conversely, the I^+ ions were emitted preferentially in the backward direction, and the Br^+ ions were emitted preferentially in the forward direction at $\phi = \pi$, when the electric field maximum pointed in the backward direction.

The inset in Fig. 3 shows the forward to backward yield ratio (I_f/I_b) obtained when we changed the relative phase difference between the fundamental and the second-harmonic light by rotating the quartz plate. Oscillation behavior as a function of incident angle θ is clearly observed in both the I^+ and the Br^+ signals. We carefully examined the oscillation of the signals to confirm that it was caused not by some artifact, such as fluctuation in

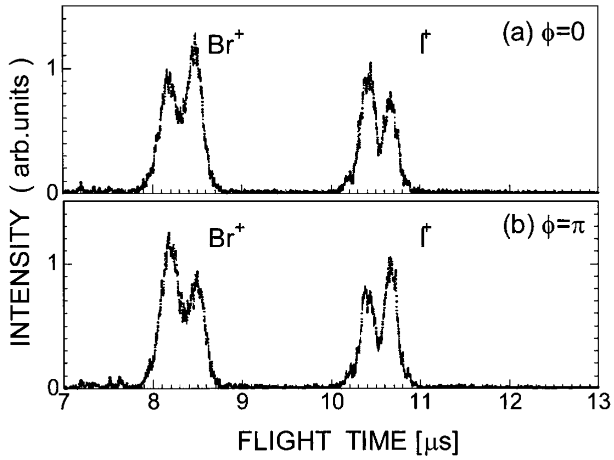

FIG. 2. TOF spectra of I^+ and Br^+ ions produced by dissociative ionization of IBr when they were irradiated with both the 800 and the 400 nm pulses at relative phase difference (a) $\phi = 0$ and (b) $\phi = \pi$.

laser intensity, but by interference between the simultaneous excitations. We optimized the intensity of the second-harmonic light to maximize the modulation depth. The relative phase difference between the ω and 2ω pulses was determined from the incident angle θ and the refractive index of the quartz plate at 400 nm ($n = 1.470$). A clear periodicity of 2π is observed in the I_f/I_b ratio. Moreover, the phase dependence of the Br^+ signal is completely out of phase with that of the I^+ signal. This result shows that directional separation of the photofragments was achieved. To our knowledge, this is the first observation of directional separation in photodissociation using phase-controlled $\omega + 2\omega$ optical fields.

One possible explanation for the out-of-phase behavior is a phase lag π between the $IBr^+ \rightarrow I^+ + Br$ and $IBr^+ \rightarrow I + Br^+$ channels. Such a phase lag has been observed in the control of the branching ratio between photoionization and photodissociation using the $\omega + 3\omega$ scheme [9]. The phase lag between the photodissociation and photoionization channels is caused by molecular phase, and the phase lag can be continuously changed by detuning from the resonant transition. We tested this possible explanation by changing the wavelength from 795 to 805 nm. We could not find any resonance effect, and the I^+ and Br^+ ions maintained their out-of-phase behavior. Therefore, we can rule out the possibility of a phase lag caused by resonant effects.

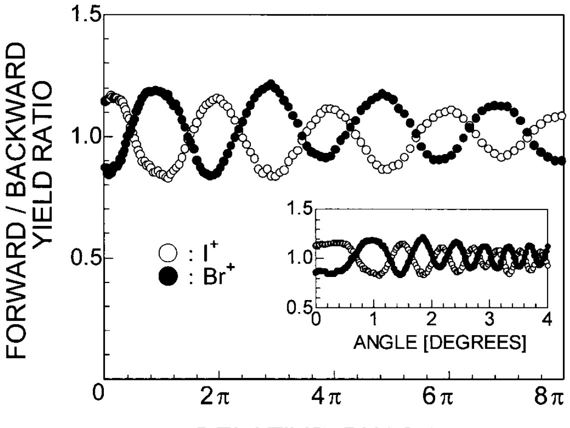

FIG. 3. The forward/backward yield ratio (I_f/I_b) as a function of relative phase difference ϕ: (open circles) iodine ion; (solid circles) bromine ion. The inset shows the forward/backward yield ratio as a function of the angle (θ) of the phase-shifting plate.

The only explanation for the out-of-phase behavior observed in the I_f/I_b ratio is that the phase-controlled $\omega + 2\omega$ optical field produced a molecular orientation in which the laser fields discriminated between parallel and antiparallel molecular configurations. The molecular orientation leads to antiphase behavior between the I^+ and Br^+ ions with directional asymmetry. Experimental results indicate that the direction of the permanent dipole for IBr molecules is parallel to the direction of the optical field when the electric field maximum points toward the detector at $\phi = 0$.

Recent investigations of molecular alignment have focused on the question of whether observed fragment-ion angular distributions result from laser-induced alignment of molecules during the dissociative ionization process (dynamic alignment) or the angular dependence of the ionization process (geometric alignment) [21,22]. We can extend this discussion to the molecular orientation, that is to say whether the orientation is geometric or dynamic.

Early theoretical work on dynamic orientation pointed out that the key parameter is the wavelength of the laser field that interacts with the permanent dipole. There are two regions with respect to the laser wavelength [15]. In the long-wavelength region (10 μm for HD^+), an efficient interaction between the permanent dipole and the electric fields induces a molecular orientation within one optical cycle, which is analogous to the static field picture. A similar effect has been investigated theoretically in the two-frequency IR laser orientation of polar molecules [24]. In the short-wavelength region, by contrast, the fast optical period averages to zero over the optical cycle and the effect of the permanent dipole disappears. This leads not to molecular orientation but to alignment of the induced dipole, as observed experimentally in HD^+ molecules [16].

Recent theoretical work concerning molecular orientation induced by laser fields has produced significant results. The interaction between permanent dipoles and laser fields in the high-frequency region has been investigated [25]. The first-order interaction between a permanent dipole and a laser field averages to zero over the optical cycle. By contrast, the second-order interaction between a permanent dipole and a laser field averages to a finite value over the optical cycle and thus contributes to molecular alignment. Keller *et al.* have suggested that dynamic molecular orientation in the high-frequency region can be achieved by using phase-controlled $\omega + 2\omega$ optical fields, which supports our experimental results using $\lambda = 400$ and 800 nm [25].

There have been no theoretical predictions of the geometric-orientation effect induced by phase-controlled $\omega + 2\omega$ optical fields in the short-wavelength region. Qualitatively, the enhancement of orientation-dependent ionization probability is in good agreement with the simple double-well-potential model [26]. Theoretical work on the geometric-orientation effect remains to be done. In many cases, geometric and dynamic orientation should coincide. In IBr molecules, geometric-orientation dominates for subpicosecond pulses, and it does for I_2 and Br_2 [22]. Further studies, such as double-pulse experiments, are required if we are to distinguish between geometric and dynamic orientation [27].

In conclusion, we have investigated coherent control of the dissociative ionization of IBr using phase-controlled two-color laser pulses. Our experiment shows two significant results: (i) molecular orientation can be achieved with only optical fields; (ii) the direction of the orientation is completely controlled by the sign of the interference. Recently, clear evidence of molecular orientation induced by combined electrostatic and laser fields has been demonstrated [28]. To achieve molecular orientation more clearly, two more experiments are available: (i) the use of dynamic orientation effects for lighter molecules such as CO and NO and (ii) the use of a linearly polarized pump (aligning) pulse and a circularly polarized probe pulse [27]. Recently, absolute-phase phenomena in photoionization with few-cycle laser pulses have been observed; in this case, it makes a difference whether the atoms feel the fast force in the positive or the negative direction [29]. Few-cycle laser pulses and phase-controlled optical fields are characteristic of the asymmetry with respect to the direction of electric fields. These phase-controlled laser fields may produce complete reaction control.

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