

Robust quantum control of molecular tunneling ionization in the space domain by phase-controlled laser fields

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Quantum control of a system with coherent laser fields involves not only a time-domain component but also a space-domain component. Here we used phase-controlled laser fields to achieve quantum control of tunneling ionization in the space domain and the resultant selective ionization of oriented molecules in the gas phase. The directionally asymmetric tunneling ionization induced by intense (5.0×10^{12} W/cm²) nanosecond phase-controlled fields consisting of a fundamental light and second-harmonic light led to selective ionization of oriented molecules, which reflects the geometric nature of the highest occupied molecular orbital in the ground state. High selectivity was achieved with a single control variable. Quantum control was robust, being free of both laser wavelength and pulse-duration constraints, and thus can be applied to a wide range of molecules. Moreover, the combination of a conventional laser source and an adjustment-free simple optical system provided robust quantum control with high reproducibility.

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Quantum control or coherent control—the direct manipulation of the wave function and its quantum dynamics through the coherent nature of a laser field—is a fascinating method for maximizing the property or function of matter and the selectivity of a chemical reaction [1–4]. The principle of quantum control is to selectively induce transitions from the ground state to a manifold of targeted excited states and then steer their quantum dynamics in the time domain toward the desired outcome by using constructive or destructive quantum interference effects [1–4]. Initially, quantum control was applied to simple systems such as atoms and diatomic molecules. In these early proof-of-principle demonstrations, only a single parameter, such as the relative phase between two laser fields [4–6] or the time delay between two laser pulses [4,7,8], was varied. Subsequently, the advent of closed-loop optimal control using femtosecond shaped-pulses allowed researchers to deal with complex systems by simultaneously varying multiple laser parameters at the wavelengths employed [9,10]. Despite the expected complexity associated with this multiparameter approach, many experiments have proven that it is easier to optimize the targeted objective than one might expect [4,11,12]. Fine-tuned manipulation of quantum dynamics in the time domain has increasingly become significant for maximizing the property or function of matter.

Quantum control involves not only a time-domain component but also a space-domain component. Molecules are randomly oriented in the gas or liquid phase, and light-matter interaction depends on the relative orientation between the molecular geometry and the polarization direction of the irradiating light. This orientation dependence can lead to undesired excited states or steer the quantum dynamics differently for each molecule, leading to ambiguous optimization or selectivity. So far, only a few researchers have used closed-loop optimal control of polarization shaping for quantum control of molecular systems in the space domain [13,14]. Recently, we have employed intense (10^{12} – 10^{13} W/cm²) femtosecond phase-controlled two-color la-

ser fields consisting of a fundamental light and second-harmonic light (hereafter the $\omega+2\omega$ scheme) to achieve quantum control of tunneling ionization in the space domain and the resultant selective ionization of oriented molecules (SIOM) in the gas phase [15]. In this paper, by using intense (5.0×10^{12} W/cm²) nanosecond phase-controlled $\omega+2\omega$ laser fields we show that the SIOM induced by directionally asymmetric tunneling ionization is robust quantum control.

The principle of the $\omega+2\omega$ scheme has been described previously [15]. 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 ω and 2ω pulses. The phase-controlled $\omega+2\omega$ field has a characteristic asymmetry: The amplitude of the electric field in the positive (left) direction is twice that in the negative (right) direction when $\phi=0$ and $E_1=2E_2$ [Fig. 1(1)]. The directional asymmetry is reversed when $\phi=\pi$ [Fig. 1(2)]. The directional asymmetry of the electric field is independent of t and dependent only on ϕ [16]. Phase-dependent phenomena induced by phase-controlled $\omega+2\omega$ fields have been observed in a variety of systems [17]. Directionally asymmetric tunneling ionization in atoms was first investigated by Muller *et al.* [18,19]. Tunneling ionization is induced by removing an electron through the suppressed potential barrier of the combined nuclear field and laser fields. For monochromatic laser fields with a symmetric waveform, electrons are removed at the same rate from the atoms in both the negative and positive directions along the laser polarization. In contrast, when atoms are ionized by phase-controlled $\omega+2\omega$ laser fields with an asymmetric waveform, electrons are much more strongly removed by the tunneling process opposite to the direction of the electric field vector at its maxima. Recently, using phase-stabilized few-cycle pulses, Paulus *et al.* observed directionally asymmetric tunneling ionization in atom photoionization [20].

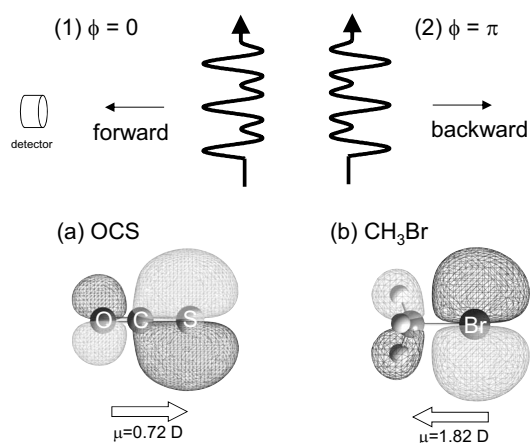


FIG. 1. Wave forms of phase-controlled two-color $\omega+2\omega$ laser fields at a relative phase difference of (1) $\phi=0$ and (2) $\phi=\pi$. We define the relative phase difference as $\phi=0$ when the electric field maxima point toward the detector (forward direction) and as $\phi=\pi$ when the electric field maxima point away from the detector (backward direction), (a), (b) Molecular structures and isocontours of the HOMOs of (a) OCS and (b) CH_3Br . The shadings indicate the signs of the wave functions. The directions of the permanent dipoles are shown by thick arrows.

Molecular ionization in intense laser fields can be described by the molecular Ammosov-Delone-Krainov (ADK) model, in which electrons are removed from the highest occupied molecular orbitals (HOMOs) via the tunneling process [21,22]. The molecular structures and isocontours of the HOMOs of carbonyl sulfide (OCS) and methyl bromide (CH_3Br) are shown in Figs. 1(a) and 1(b), respectively. The HOMOs were determined by *ab initio* calculations using the Gaussian 03W software package [23] [method: MP2; basis sets: 6-311++G(3df,2pd)]. The ionization potential and permanent dipole of OCS are 11.18 eV and 0.72 D, whereas those of CH_3Br are 10.54 eV and 1.82 D [24]. The HOMOs of both molecules show an asymmetric π structure. According to the molecular ADK model, ionized electrons are much more strongly extracted via the tunneling process from the large-amplitude part of the HOMO along the opposite direction of electric field vector [21,22]. When tunneling ionization of molecules is induced by $\omega+2\omega$ fields, molecules oriented in the direction shown in Figs. 1(a) and 1(b) would be much more strongly ionized by $\omega+2\omega$ fields at $\phi=0$ than those oriented in the opposite direction. Both the asymmetries of the waveforms of the laser fields and the structure of the HOMO play essential roles in the discrimination of the head-to-tail order of the molecules. Several groups have used the intense-field $\omega+2\omega$ scheme to investigate the ionization of hydrogen molecules [25]. Recently, we investigated the SIOM induced by phase-controlled $\omega+2\omega$ fields with a pulse duration of 130 fs and an intensity of 10^{12} – 10^{13} W/cm² [15]. In this paper, we investigate the SIOM induced by *nanosecond* phase-controlled $\omega+2\omega$ laser fields. As shown in Figs. 1(a) and 1(b), the geometry of the HOMO and direction of the permanent dipole of OCS are different from those of CH_3Br . The permanent dipole of OCS points from the small-amplitude part (O) to the large-amplitude part (S) of the wave function. In contrast, the permanent dipole of CH_3Br

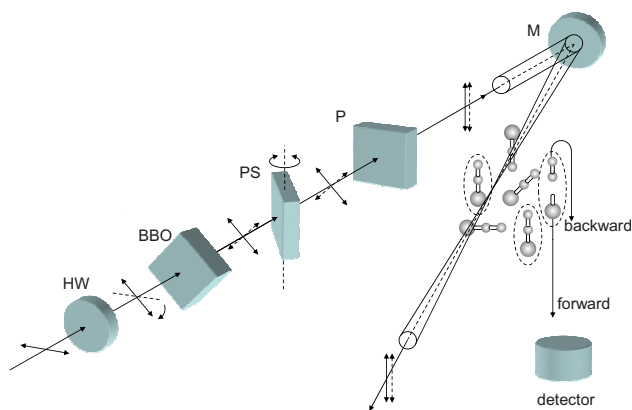


FIG. 2. (Color online) Schematic of the optics set generating the phase-controlled $\omega+2\omega$ laser fields. The elements are labeled as follows: HW, half-wave plate; BBO, frequency-doubling crystal; PS, phase shifter; P, polarizer; M, dielectric concave mirror. The polarization of the fundamental (second harmonic) light is shown as solid (dotted) double-headed arrows.

points from the large-amplitude part (Br) to the small-amplitude part (CH_3) of the wave function. Later in this paper, we will use this difference to determine the mechanism of the orientation process. Light absorption starts at about 255 nm for OCS and 285 nm for CH_3Br respectively; thus there is no resonance of ω , 2ω , and 3ω with any electronic transition [26].

The experimental setup consisted of a pulsed Nd:YAG laser, an optical system generating phase-controlled laser fields, and a time-of-flight mass spectrometer (TOF MS) equipped with a supersonic molecular beam source. The *Q*-switched Nd:YAG laser (Spectra-Physics, LAB150) generated horizontally polarized, 10-ns-duration, 1-cm^{-1} -bandwidth laser pulses at a 1064 nm wavelength and was operated at a repetition rate of 10 Hz without injection seeding. Note that we made no attempt to improve either the temporal profile or the spatial profile of the laser beam even though it was spectrally and temporally multimodal. The optics set generating the phase-controlled laser pulses consisted of only five components (Fig. 2) and is similar to Schumacher's setup [19]. After the fundamental light passed through a half-wave plate that rotated its polarization direction by -45° , 532-nm second-harmonic pulses polarized to 45° were produced by a frequency-doubling crystal [β -barium borate (BBO), type I phase-matching, 10 mm thickness, conversion efficiency: 30%]. Both the fundamental pulse and second-harmonic pulse passed through a phase-shifting quartz plate (10 mm thickness) that could be rotated around the incident angle of 45° to control the relative phase difference ϕ between the ω and 2ω pulses. The relative phase difference was calibrated by Schumacher's procedure [19]. Then the vertical polarization component of the ω and 2ω pulses was selectively transmitted by a polarizer for a high-power laser (air-spaced Glan-Thompson prism). The total intensity $I=I_1+I_2$ was 5.0×10^{12} W/cm² and the I_2/I_1 ratio was around 0.25 ($E_2/E_1=0.5$), where I_1 and I_2 are the intensities of the ω and 2ω pulses. Finally, the phase-controlled $\omega+2\omega$ pulses were focused on the molecular beam in the TOF-MS by a dielec-

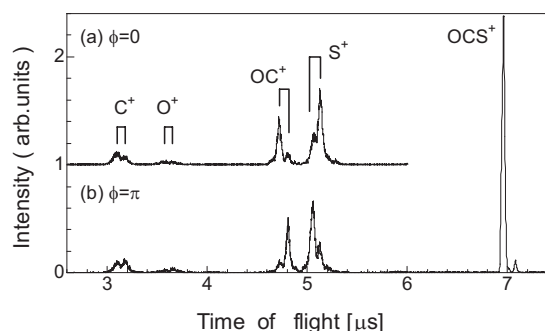


FIG. 3. TOF spectra of the singly-charged ions produced by dissociative ionization of OCS molecules irradiated with phase-controlled two-color $\omega+2\omega$ laser fields at the relative phase differences (a) $\phi=0$ and (b) $\phi=\pi$. The solid lines indicate pairs of forward and backward peaks.

tric concave mirror for 1064 and 532 nm with a damage threshold of 2 J/cm^2 . Note that both temporal and spatial overlap of the two beams is ensured without optics adjustment because the difference in propagation delay between the ω and 2ω pulses ($<4 \text{ ps}$) is much smaller than the coherence time (40 ps) and the difference of lateral walkoff between the ω and 2ω pulses after passing through the phase-shifting plate ($<50 \text{ }\mu\text{m}$ with respect to the 8 mm laser beam diameter) is negligible. Furthermore, this optics set does not require interferometric stability because phase fluctuations in the ω and 2ω beams cancel out when the beams pass through the same path. Our interferometer-free optics set allowed us to use a compact unit to generate phase-controlled $\omega+2\omega$ laser fields without a vibration isolation system. Finally, combination of a conventional laser source and an adjustment-free simple optical system provided robust quantum control with high reproducibility.

A TOF-MS equipped with a pulsed supersonic molecular beam source was used to detect the ionized molecules and their photofragments. The target gas for the molecular beam was diluted (5%) with helium gas to obtain a total pressure of $5.0 \times 10^4 \text{ Pa}$. With 10 Hz operation of the pulsed molecular beam, the pressure in the TOF-MS was kept below $1.0 \times 10^{-5} \text{ Pa}$. The polarization direction of the phase-controlled $\omega+2\omega$ pulses was set to be parallel to the TOF axis and perpendicular to the molecular beam. The TOF-MS was a conventional two-stage Wiley-McLaren type spectrometer (kinetic energy resolution: 0.05 eV).

Figure 3 shows the TOF spectra of singly charged OC^+ , S^+ , and parent OCS^+ ions produced when OCS molecules were irradiated with phase-controlled $\omega+2\omega$ pulses. All photofragments exhibited a pair of peaks. The first peak resulted from ions ejected directly toward the detector, and the second from ions that were first ejected in the backward direction before being accelerated toward the detector by the extraction field. The spacing between the forward and backward peaks reflects the kinetic energy release. The kinetic energies of the photofragments were $0.49 \pm 0.05 \text{ (C}^+)$, $0.65 \pm 0.05 \text{ (O}^+)$, $0.37 \pm 0.05 \text{ (OC}^+)$, and $0.20 \pm 0.05 \text{ (S}^+)$ eV. The relative yields of OC^+ , S^+ , and OCS^+ were independent of laser intensity in the intensity range we investigated. If the pathway involving ionization of neutral fragments pro-

duced by dissociation of neutral OCS molecules made a substantial contribution to the reaction pathway, the relative yields of the three ions would not have been constant. Thus, the main pathway for dissociative ionization was as follows: $\text{OCS} \rightarrow \text{OCS}^+ \rightarrow \text{OC}^+ + \text{S}$ or $\text{OC} + \text{S}^+$. The contribution of the pathway involving the postionization of neutral fragment dissociated from neutral OCS molecules can be expected to be negligible, although a laser pulse duration of 10 ns might be sufficiently long to induce the post-ionization process. The contribution of the dissociation pathway via Coulomb explosion, $\text{OCS} \rightarrow \text{OCS}^{2+} \rightarrow \text{OC}^+ + \text{S}^+$, was also negligible, for two reasons: (i) The experiment was performed at a laser intensity below that at which the formation of OCS^{2+} and doubly charged fragment ions were observed and (ii) the observed kinetic energies of the OC^+ and S^+ ions were much smaller than those expected for a Coulomb explosion process ($>3 \text{ eV}$).

We are aware of the controversy concerning the boundary between multiphoton ionization and tunneling ionization. Keldysh first suggested that an increase in laser intensity causes a transition from multiphoton ionization to tunneling ionization [27]. The Keldysh parameter, $\gamma = (2\omega^2 I_p / I)^{1/2}$, is used to judge whether a phenomenon involves multiphoton ionization or tunneling ionization, where ω and I are the field frequency and intensity, and I_p is the ionization potential of the matter. If $\gamma > 1$, then multiphoton ionization is dominant; if $\gamma < 1$, then tunneling ionization is dominant. Because there is no absolute boundary between multiphoton ionization and tunneling ionization, phenomena that fall in the intermediate region ($\gamma \sim 1$) can often be successfully explained by both multiphoton ionization and tunneling ionization. Our experimental condition corresponds to $\gamma \sim 2$. Recent theoretical and experimental studies have shown that tunneling ionization remains the dominant ionization mechanism even at $\gamma \sim 3$ [28].

The breaking of the forward-backward symmetry was clearly observed in the TOF spectrum. The forward peak of the CO^+ ions predominated at $\phi=0$. This result shows that the CO^+ ions were preferentially ejected toward the detector at $\phi=0$ when the electric field maxima pointed toward the detector. Conversely, the backward peak of the S^+ ions predominated at $\phi=0$. This behavior was reversed by changing the relative phase difference $\phi=0$ to $\phi=\pi$. The C^+ and O^+ ions also showed forward-backward asymmetry.

Despite the experimental condition having been far from interferometric stability, a clear periodicity of 2π with a considerably large contrast was observed in the ratio of the forward to backward yields (I_f/I_b), obtained when we changed the relative phase difference between the ω and 2ω pulses by rotating the phase-shifting quartz plate (Fig. 4). The OC^+ and the S^+ cations were completely out of phase with each other. This result shows that oriented molecules were detected with discrimination of their head-to-tail order. The selectivity of oriented molecules from the OC^+ cations reached 86% ($I_f/I_b=5.9$), whereas that from the S^+ cations reached 76% ($I_f/I_b=3.2$), without further improvement of either the temporal or spatial profile of the laser beam. The C^+ and O^+ cations were completely in phase with OC^+ , indicating that the molecules were detected with preservation of the O-C-S molecular structure.

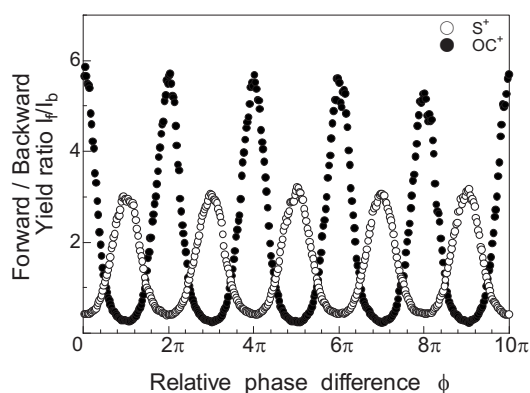


FIG. 4. Forward-to-backward yield ratio (I_f/I_b) as a function of relative phase difference ϕ : open circles, S^+ cation; closed circles, OC^+ cation.

We now discuss the orientation process induced by the phase-controlled $\omega+2\omega$ fields from the direction of the observed molecular orientation. In theoretical investigations, Dion *et al.* [29] and Guérin *et al.* [30] showed that phase-controlled $\omega+2\omega$ fields can induce dynamical molecular orientation (DMO). In DMO, molecules can be dynamically oriented along the laser polarization direction by the torque generated by the *nonlinear* interaction between a nonresonant laser field and the permanent dipoles of the molecules (the *linear* interaction averages to zero over an optical cycle even in an $\omega+2\omega$ laser field, and thus cannot orient molecules) [29,30]. We performed simultaneous measurements using gas mixtures of OCS and reference CH_3Br to discriminate whether the orientation process is SIOM or DMO [the permanent dipole of OCS (CH_3Br) points from the large-amplitude part (small-amplitude part) to the small-amplitude part (large-amplitude part) of the wave function [15]]. The experimental result showed that SIOM is the main contributor to the orientation process rather than DMO, where the S^+ in OCS and Br^+ in CH_3Br were completely in phase with each other. Even for nanosecond pulses, which have sufficient time to interact with molecules, SIOM is the main contributor to the orientation process, and experiments using femtosecond $\omega+2\omega$ (400+800 nm) pulses gave a similar result [15]. We have experimentally confirmed that SIOM induced by directionally asymmetric tunneling ionization is free of laser wavelength constraints and is observed univer-

sally in the wide range of pulse duration from the femtosecond to nanosecond regime. On the other hand, several researchers have confirmed that molecules can be dynamically aligned in intense nanosecond laser fields (without discriminating the head-to-tail order of the molecules) through the *linear* interaction between nonresonant laser fields and *induced* dipoles [31]. Therefore, it is reasonable to conclude that our intense nanosecond $\omega+2\omega$ laser field induces SIOM in dynamically aligned molecules, rather than in randomly oriented molecules, during the laser pulse. Although the experimental results showed that SIOM was the main contributor to the orientation process, the quantitative contribution of DMO remains unclear. Additionally, to observe the contribution of pure DMO induced by a nanosecond $\omega+2\omega$ laser field, we carried out a double-pulse experiment involving an orienting nanosecond $\omega+2\omega$ pulse and a delayed femtosecond probe (ionization) pulse. We have not yet succeeded in observing the forward-backward asymmetry due to DMO in the double-pulse experiment. The contribution of DMO would be expected to observe if the molecules are initially cooled to a rotational temperature in the range below a few Kelvin [31].

Why is this quantum control so robust? The reason is that quantum control of tunneling ionization is independent of the excited state and details of its quantum dynamics, as shown by the fact that the quantum control was free of excitation wavelength and pulse-duration constraints. Additionally, this reason is also supported by the fact that high selectivity was achieved with a single control variable even though laser field quality was far from the best; it is well known that the temporal profile of a multimodal nanosecond Nd:YAG laser pulse has a noisy waveform with many spike structures. A higher class of quantum control such as high-harmonics generation and attosecond pulse generation will require delicate multiparameter closed-loop optimal control [32] because the complicated quantum dynamics of ionized electrons synchronized with an oscillating laser field, known as the “rescattering process” [33], must be considered. Quantum control in the spatiotemporal domain should lead to complete maximization of the property or function of matter and selectivity of a chemical reaction.

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