Selective Ionization of Oriented Nonpolar Molecules with Asymmetric Structure by Phase-Controlled Two-Color Laser Fields

Hideki Ohmura,[1,2] Naoaki Saito,[1] and M. Tachiya[1]

[1]*National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan*
[2]*PRESTO, Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan*

(Received 2 December 2005; published 1 May 2006)

We report on the selective ionization of oriented nonpolar molecules with asymmetric structure by using phase-controlled two-color $\omega + 2\omega$ laser pulses with an intensity of 1.0×10^{13} W/cm^2 (tunneling ionization regime) and a pulse duration of 130 fs. The orientation of 1-bromo-2-chloroethane was monitored by the directional asymmetries of the forward-backward emission in dissociative ionization. The observed direction of orientation clearly confirms that molecular orientation is induced not by dynamic orientation but by selective ionization of oriented molecules, which reflects the structure of the highest occupied molecular orbital. This method can be applied for the vast majority of molecules.

DOI: 10.1103/PhysRevLett.96.173001 PACS numbers: 33.80.Gj, 42.50.Hz

Recent advances in the molecular manipulation of the gas phase by intense laser fields, such as alignment (which does not discriminate between head and tail order of molecules) or orientation (which does discriminate between head and tail order of molecules), have enabled us to achieve precision spectroscopy, nanoscale design, or chemical reaction control because the orientational averaging that leads to loss of information or disturbs the homogeneous molecular manipulation can be eliminated (for a review, see Ref. [1]). In general, the effects regarding molecular alignment or orientation include two main contributions: (1) dynamic molecular alignment or orientation—molecules can be dynamically aligned or oriented along the laser polarization direction by the torque generated by the interaction between nonresonant laser fields and the dipole moment (induced dipole or permanent dipole) of molecules; (2) selective ionization of aligned/oriented molecules—molecules initially aligned or oriented in a certain direction with respect to the laser polarization have large ionization rates, resulting in selective ionization of aligned/oriented molecules in randomly oriented molecular ensembles.

Dynamic molecular alignment or orientation is preferred for applications such as nanoscale design or chemical reaction control because all molecules within a laser-irradiated volume can be aligned or oriented. The alignment of molecules by a polarized single-frequency laser field has been investigated extensively [2–5]. If the laser pulse is longer than the rotational period of the molecules, then molecules align adiabatically during laser irradiation [2]. If the laser pulse is shorter than the rotational period of the molecules, then rotational wave packets are formed and dynamical alignment is reconstructed at revival times even after the laser irradiation [3,4]. A recent theoretical investigation has analyzed the crossover between the long-pulse adiabatic limit and the short-pulse impulsive limit [5]. In general, however, single-frequency laser fields with waveforms symmetric with respect to the negative and positive directions along the laser polarization can align but cannot orient molecules while discriminating the head-tail order because the interaction with the permanent dipole averages to zero over the optical cycle. Other recent theoretical investigations have proposed that double-frequency (two-color) laser irradiation can achieve molecular orientation [6–8]. (For molecular orientation by using dc electric fields, see Ref. [9], and for a proposal to use specially tailored laser pulses or half-cycle pulses, see Ref. [10] and references therein.) The method studied here employs phase-controlled two-color laser pulses: a fundamental pulse and a second-harmonic pulse (hereafter referred to as the $\omega + 2\omega$ scheme). We have experimentally investigated molecular orientation by using phase-controlled $\omega + 2\omega$ laser pulses [11,12]. Even for the $\omega + 2\omega$ scheme, however, applicable molecules are limited because we cannot orient nonpolar molecules with asymmetric structure, as this method is based on the interaction between laser fields and permanent dipoles.

On the other hand, selective ionization of aligned or oriented molecules is available for precision measurement where we can eliminate orientational averaging by detecting only oriented molecules in an ensemble of randomly oriented molecules. Theoretically, selective ionization of aligned molecules in intense laser fields can be described by the molecular Ammosov-Delone-Krainov (ADK) model [13], which takes into account the tunnel ionization from the highest occupied molecular orbital (HOMO), or the molecular Keldysh-Faisal-Reiss model [14] in terms of molecular ionization rates modified by the interference from the atoms' centers. Recent experimental investigation has shown the availability of selective ionization of aligned molecules, in which the fragment-emission pattern of molecules aligned to a certain axis with respect to the direction of laser polarization reflects the structure of the HOMO [15]. Selective ionization of aligned or oriented molecules has the potential for directly imaging the wave function [16] as the ultimate measurement in randomly oriented molecules. So far, experiments for selective ionization have tested aligned molecules and have not discriminated the head-tail order of molecules in single-frequency laser fields [15]. Experiments should next focus on the selective ionization of oriented molecules. As with dynamic molecular orientation, however, a single-frequency laser field—with a waveform that is symmetric with respect to the negative and positive directions along the laser polarization—cannot discriminate the head-tail order because the ionization rate of molecules with negative orientation along the direction of polarization is equal to the rate of those with positive orientation.

In this Letter, we show that an asymmetric waveform of phase-controlled double-frequency laser fields can selectively ionize oriented nonpolar molecules with asymmetric structure as a consequence of tunnel ionization, which reflects an asymmetric HOMO structure.

Our strategy for selective ionization of oriented molecules is shown schematically in Fig. 1. 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 negative (right) direction is twice that in the positive (left) direction when $\phi = \pi$ and $E_1 = 2E_2$ [Fig. 1(a)] [8]. The directional asymmetry can be flipped by $\phi = 0$ [Fig. 1(b)]. The molecular ionization in intense laser fields described by the molecular ADK model is based on the tunnel ionization of an electron through the suppressed potential barrier of the combined nuclear field and laser fields [13]. In the case of monochromatic laser fields with a symmetric waveform, electrons are removed from the molecules in both the negative and positive directions along the laser polarization at the same rate. On the other hand, when the molecules are ionized by phase-controlled $\omega + 2\omega$ laser fields, electrons are much more strongly removed by the tunneling process from the side of the molecule opposite to the direction of the electric field vector at its maxima. This phenomenon has been observed in atom photoionization by using phase-controlled $\omega + 2\omega$ laser fields and phase-stabilized few-cycle pulses [17,18].

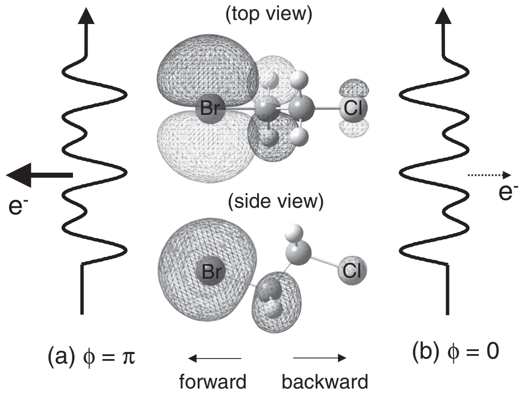

FIG. 1. Waveform of phase-controlled two-color $\omega + 2\omega$ laser fields at relative phase differences (a) $\phi = \pi$ and (b) $\phi = 0$, with molecular structures and isocontours of the HOMO of 1-bromo-1-chloroethane. The different shadings indicate different signs of the wave functions. We 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).

As an example of a nonpolar molecule with asymmetric structure, we have chosen 1-bromo-2-chloroethane (BCE) (ionization potential: 10.55 eV) [19]. Figure 1 shows the molecular structure and HOMO of BCE as determined by *ab initio* calculations using the Gaussian 03W software package [method, MP2; basis set, $6\text{–}311 + G(d, p)$]. The trans isomer shown in Fig. 1 is most stable in the gas phase among the three possible rotational isomers. The BCE molecule has a very small permanent dipole moment (calculated value: 0.0057 D, pointing from Cl to Br) due to the cancellation of two halogen atoms with large electronegativities (Cl, 3.0; Br, 2.8) located on opposite sides of the molecule. On the other hand, the HOMO shows π structure with large asymmetry along the molecular frame (Fig. 1). Thus we can derive the contribution induced by the asymmetric HOMO structure while minimizing the effect of dynamic orientation.

According to the molecular ADK model, ionized electrons are much more strongly extracted via the tunneling process from electronic clouds along the direction of electric fields [13]. When tunneling ionization of BCE molecules is induced by $\omega + 2\omega$ fields at $\phi = \pi$, electrons are much more likely to be removed from the Br side of the molecules. As a result, BCE molecules oriented in the direction shown in Fig. 1 would be much more strongly ionized by $\omega + 2\omega$ fields at $\phi = \pi$ than those oriented in the opposite direction. Both the asymmetries of the waveforms of the laser fields and the HOMO structure play essential roles in the discrimination of the head-tail order of the molecules.

The experimental apparatus, which has been described previously [12], consisted of a Ti:sapphire laser system, a Mach-Zehnder interferometer (MZI), and an ion time-of-flight (TOF) mass spectrometer. Here, we have added supplementary information, especially about how to handle the 130-fs, $\omega + 2\omega$ (800 and 400 nm) laser pulses with the MZI. The conversion efficiency of the 0.5-mm thick β-BaB_2O_4 (BBO) crystal used for frequency doubling is 30%. The I_2/I_1 ratio was adjusted by rotating the phase-matching angle of the BBO crystal while keeping the total intensity $I = I_1 + I_2$ constant, where I_1 and I_2 are the intensities of the ω and 2ω pulses, respectively. The MZI consisted of standard mirror mounts and a doubly stacked standard breadboard mounted to an optical table isolated by rubber dampers. The MZI was placed in an enclosure system that is not airtight (not in a vacuum). We did not use any active controls for mechanical vibrations.

To compensate for the fluctuations generated from any cause, we performed simultaneous measurements between target molecules and reference molecules (CH_3I) by using gas mixtures [12]. By sorting the data along with the reference data, the MZI effectively achieved a resolution of 30 asec. The gas sample for the molecular beam was prepared by passing He gas over liquid BCE (Lancaster, 95%) to create a pressure of 0.1 MPa.

The TOF mass spectrum obtained from excitation of BCE molecules with the ω pulses alone is shown in Fig. 2. Various single-charged ions were detected. We believe that tunneling ionization is the dominant process because the experiment was performed with a laser intensity (10^{13} W/cm^2) in the vicinity of the regime where doubly charged fragment ions due to Coulomb explosion were observed. The parent BCE^+ ions show triple sharp peaks due to the bromine isotopes ^{79}Br and ^{81}Br, and the chlorine isotopes ^{35}Cl and ^{37}Cl (two peaks overlap each other among the four peaks). Both Br^+ and Cl^+ show a pair of peaks: one peak corresponds to ejection toward the detector (forward direction), and the other peak corresponds to ejection away from the detector (backward direction). The spacing of the forward and backward peaks reflects the kinetic energy of the photofragments after dissociation. The observed kinetic energies were 1.5 eV (1900 m/s) for Br^+ and 4.0 eV (4700 m/s) for Cl^+. Other fragment ion peaks were not split forward or backward but were broad because of small kinetic energies (< 0.5 eV), which come from energy partitioning between translational and internal (vibration and rotation) modes [20].

When BCE molecules were irradiated by both the ω and 2ω pulses with zero time delay, directional asymmetries in the forward-backward emissions were observed in the TOF spectrum. We obtained ratios of the forward and backward yields, I_f/I_b, by changing the relative phase difference between the ω and the 2ω pulse (Fig. 3). From the $Br(CH_2)_2^+$ and $(CH_2)_2Cl^+$ peaks, which were not clearly split into forward-backward peaks, we obtained the I_f/I_b ratio from the area of the forward and backward sides with respect to the peak center. A clear periodicity of 2π was observed in the I_f/I_b ratio for all photofragments displayed. We optimized the I_1/I_2 ratio to maximize the modulation depth, and the largest contrasts were observed when the I_2/I_1 ratio was around $0.25(E_2/E_1 = 0.5)$. The phase dependencies between the Cl^+ (Br^+) ions and countercations were completely out of phase with each other. This result shows that phase-controlled $\omega + 2\omega$ fields can discriminate the molecular orientation from the head-tail order. Moreover, the phase dependencies between Cl^+ and Br^+ were also out of phase with each other. It is evident from all phase dependencies that phase-controlled $\omega + 2\omega$ fields discriminate the molecular orientation of the head-tail order.

We now discuss the orientation process induced by the phase-controlled $\omega + 2\omega$ fields from the direction of the observed molecular orientation. In previous investigations, it was often controversial whether the observed fragment-emission patterns are the results of either dynamic molecular alignment or selective ionization of the aligned molecules [21]. Molecular orientation also involves the same problem. The permanent dipole of the BCE molecule is very small (calculated value: 0.0057 D) but is not completely zero, so that dynamic molecular orientation can be considered. The permanent dipole of the BCE molecule points from the chlorine atom to the bromine atom. The electric field of the laser forces the permanent dipole in the direction of the maximum point of the phase-controlled $\omega + 2\omega$ field. If BCE molecules are dynamically oriented by a phase-controlled $\omega + 2\omega$ field, the direction of orientation should be opposite to the direction expected by the selective ionization of oriented molecules, based on the molecular ADK model [8,11,12]. We define the relative phase difference as $\phi = 0$ when the electric field maxima pointed toward the detector and as $\phi = \pi$ when the optical electric field maxima pointed the other way. The Br^+ ions were preferentially emitted toward the detector, and the Cl^+ ions were preferentially emitted away from the detector at $\phi = \pi$ when the electric field maxima pointed in the backward direction. The observed phase relation was confirmed experimentally by simultaneous measurement using gas mixtures of BCE and reference CH_3I molecules with

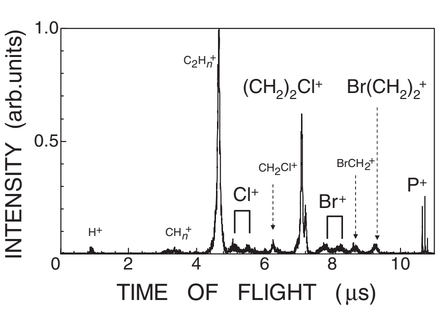

FIG. 2. (a) TOF mass spectra of ions produced by dissociative ionization of 1-bromo-2-chloroethane molecules irradiated only with 800-nm pulses. The parent molecules are denoted by "P." The solid lines indicate the pair of forward and backward peaks for Cl^+ and Br^+.

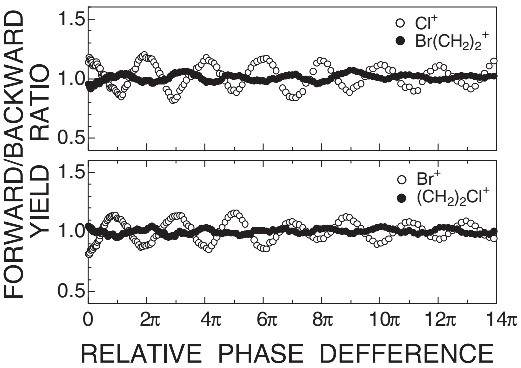

FIG. 3. Forward or backward yield ratio (I_f/I_b) as a function of relative phase difference, ϕ: (open circles) halogen ion; (solid circles) countercation.

high-dipole moment, where the Br^+ in the BCE and the I^+ in the CH_3I are in phase with each other [12]. If molecules are dynamically oriented due to their permanent dipole, then the Cl^+ in BCE and the I^+ in CH_3I have in-phase behavior. Experimentally, we can clearly rule out the possibility of dynamic molecular orientation. Observed results show that the direction of the detected molecules is consistent with that expected by the molecular ADK model, where the BCE molecules oriented in the direction shown in Fig. 1 are much more strongly ionized by the phase-controlled $\omega + 2\omega$ field at $\phi = \pi$ than at $\phi = 0$. Therefore, we conclude that the phase-controlled $\omega + 2\omega$ field achieves selective ionization of oriented molecules, reflecting the asymmetry of the HOMO structure.

Finally, we mention the relative angle between the oriented molecules and the polarization direction of the laser fields, and the contribution of the induced dipole moment. Alnaser *et al.* observed a butterfly-shaped pattern reflecting the structure of π orbitals in O_2 molecules by using 8-fs optical pulses and 2D photofragment-emission pattern imaging, where the direction of selectively ionized molecules was 40° relative to the polarization direction [15]. When 35-fs pulses were used instead of 8-fs pulses, the butterfly-shaped pattern changed to a dumbbell-shaped pattern, reflecting the situation that the direction of the selectively ionized molecules was along the laser polarization due to dynamic alignment (not orientation) by the induced dipole during the laser pulse [15]. Almost all molecules experience some contribution of dynamic molecular alignment due to an induced dipole. Thus, it is possible that our 130-fs $\omega + 2\omega$ pulse induces dynamic alignment, even for relatively heavy BCE molecules, and that our measurement is a result of the selective ionization of oriented molecules in aligned molecules during the laser pulse rather than in randomly oriented molecules. At present, unfortunately, we cannot settle on either of the two possibilities because our 1D TOF method can measure only the forward or backward direction and not the angle dependence of fragment emission. 2D photofragment-emission pattern imaging would enable us to estimate the contribution of the induced dipole.

In conclusion, we have investigated the selective ionization of nonpolar molecules with asymmetric structure using phase-controlled two-color laser pulses. The observed molecular orientation is in good agreement with that expected by the molecular ADK model, where ionized electrons are removed from asymmetric HOMO via tunneling, and we can clearly rule out the dynamic orientation effect experimentally. If very short laser pulses with asymmetric waveforms are used, such as sub-10-fs $\omega + 2\omega$ pulses, phase-stabilized few-cycle pulses, or half-cycle pulses, then dynamic alignment due to the induced dipole can be avoided. The method combines such very short optical pulses with 2D imaging of the photofragment-emission patterns, and thus may serve as a universal method for direct wave function imaging of randomly oriented molecules.

This work was partially supported by the Mitsubishi Foundation, the Sumitomo Foundation, and a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (JSPS).

[1] H. Stapelfeldt and T. Seideman, Rev. Mod. Phys. **75**, 543 (2003).

[2] H. Sakai, C. P. Safvan, J. J. Larsen, K. M. Hilligsøe, K. Hald, and H. Stapelfeldt, J. Chem. Phys. **110**, 10 235 (1999).

[3] F. Rosca-Pruna and M. J. J. Vrakking, Phys. Rev. Lett. **87**, 153902 (2001).

[4] I. V. Litvinyuk, K. F. Lee, P. W. Dooley, D. M. Rayner, D. M. Villeneuve, and P. B. Corkum, Phys. Rev. Lett. **90**, 233003 (2003).

[5] R. Torres, R. de Nalda, and J. P. Marangos, Phys. Rev. A **72**, 023420 (2005).

[6] E. Charron, A. Giusti-Suzor, and F. H. Mies, Phys. Rev. Lett. **75**, 2815 (1995); J. Chem. Phys. **103**, 7359 (1995).

[7] M. J. J. Vrakking and S. Stolte, Chem. Phys. Lett. **271**, 209 (1997).

[8] C. M. Dion, A. D. Bandrauk, O. Atabek, A. Keller, H. Umeda, and Y. Fujimura, Chem. Phys. Lett. **302**, 215 (1999).

[9] T. P. Rakitzis, A. J. van den Brom, and M. H. M. Janssen, Science **303**, 1852 (2004).

[10] J. Salomon, C. M. Dion, and G. Turinici, J. Chem. Phys. **123**, 144310 (2005).

[11] H. Ohmura, T. Nakanaga, and M. Tachiya, Phys. Rev. Lett. **92**, 113002 (2004).

[12] H. Ohmura and T. Nakanaga, J. Chem. Phys. **120**, 5176 (2004).

[13] X. M. Tong, Z. X. Zhao, and C. D. Lin, Phys. Rev. A **66**, 033402 (2002); Z. X. Zhao, X. M. Tong, and C. D. Lin, *ibid.* **67**, 043404 (2003).

[14] J. Muth-Böhm, A. Becker, and F. H. M. Faisal, Phys. Rev. Lett. **85**, 2280 (2000).

[15] A. S. Alnaser, S. Voss, X.-M. Tong, C. M. Maharjan, P. Ranitovic, B. Ulrich, T. Osipov, B. Shan, Z. Chang, and C. L. Cocke, Phys. Rev. Lett. **93**, 113003 (2004); A. S. Alnaser, C. M. Maharjan, X. M. Tong, B. Ulrich, P. Ranitovic, B. Shan, Z. Chang, C. D. Lin, C. L. Cocke, and I. V. Litvinyuk, Phys. Rev. A **71**, 031403(R) (2005).

[16] J. Itatani, J. Levesque, D. Zeidler, H. Niikura, H. Pepin, J. C. Kieffer, P. B. Corkum, and D. M. Villeneuve, Nature (London) **432**, 867 (2004).

[17] D. W. Schumacher, F. Weihe, H. G. Muller, and P. H. Bucksbaum, Phys. Rev. Lett. **73**, 1344 (1994).

[18] G. G. Paulus, F. Lindner, H. Walther, A. Baltuška, E. Goulielmakis, M. Lezius, and F. Krausz, Phys. Rev. Lett. **91**, 253004 (2003).

[19] D. W. Berman, V. Anicich, and J. L. Beauchamp, J. Am. Chem. Soc. **101**, 1239 (1979).

[20] P. M. Kroger, P. C. Demou, and S. J. Riley, J. Chem. Phys. **65**, 1823 (1976).

[21] C. Ellert and P. B. Corkum, Phys. Rev. A **59**, R3170 (1999).