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Three-dimensional molecular orientation with combined electrostatic and elliptically polarized laser fields

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We report an experimental demonstration of the three-dimensional orientation of gas-phase molecules by applying the combination of an electrostatic and an elliptically polarized laser field. Three-dimensional orientation was verified using a technique in which two-dimensional ion imaging and time-of-flight mass spectrometry are complementarily used.

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Directional control of gas-phase molecules ("alignment" [1] and "orientation" [2]) provides us with an ideal anisotropic quantum system to study phenomena related to symmetry and directions of a molecule which cannot be observed with randomly oriented samples. With aligned molecules, there have already been several successful investigations concerning the relative direction of a molecule and a laser electric field vector. The effects of laser polarization on multiphoton ionization have been examined using aligned I_2 molecules in combination with optimal control of time-dependent laser polarization [3]. Quantum interference of electron de Broglie waves has been observed within a single molecule during high harmonic generation from nonadiabatically aligned molecules [4]. On the other hand, molecular orientation has enabled us to study stereodynamical effects in chemical reactions in detail [5].

Among various methods used to align or orient molecules [6–9], one of the most promising approaches makes use of the interaction between an intense nonresonant laser field and an induced dipole moment of a molecule. Theoretical works by Friedrich and Herschbach [8,9] were followed by demonstrations of one-dimensional alignment [10,11], three-dimensional alignment [12], and one-dimensional orientation [13]. As an extension of the former studies, here we report evidence of three-dimensional molecular orientation with combined electrostatic and elliptically polarized laser fields. Advanced and elaborate experiments are required to realize and confirm three-dimensional orientation as discussed in this paper. Three-dimensional orientation corresponds to the complete directional control of gas-phase molecules in the sense that all three Euler angles of a molecule are fixed in the laboratory frame [12] with the "head-versus-tail" order of molecules arranged to be in the same way. The crystal-like anisotropic nature [14] of three-dimensionally oriented gas-phase molecules will provide us with a versatile system to investigate quantum phenomena such as those associated with the symmetry of molecular orbitals.

When a molecule is exposed to both a laser field and an electrostatic field, the Hamiltonian is expressed as the sum of rotational kinetic energy H_{rot} and the interaction potential between the molecule and fields, H_{int}. The interaction potential H_{int} consists of the permanent dipole interaction potential $V_{\mu}=-\boldsymbol{\mu}\cdot\boldsymbol{E}_{\mathrm{S}}$ and the induced dipole interaction potential $V_{\alpha}=-\Sigma_{\rho,\rho'}E_{\rho}\alpha_{\rho,\rho'}E_{\rho'}/4$ [15]. Here, $\boldsymbol{E}_{\mathrm{S}}$ designates the electrostatic field, $\boldsymbol{\mu}$ the permanent dipole moment, $E_{\rho(\rho')}$ the laser field components along the space-fixed Cartesian coordinate axes $(\rho,\rho'=x,y,z)$, and α the polarizability tensor of the molecule. A linearly polarized laser field produces double-well potentials along the polarization direction. The potentials create "pendular states," where the molecular axis librates around the field axis [8,16,17]. The double-well potentials contain nearly degenerate pairs of states (tunneling doublets). For a polar molecule, an additional electrostatic field induces a strong pseudo-first-order Stark effect by coupling the tunneling doublets, which enables efficient molecular orientation [9]. On the other hand, it has been theoretically and experimentally shown that molecules can be three-dimensionally aligned using an elliptically polarized laser field; i.e., a molecular plane can be confined to the polarization plane with the molecular axis with the largest polarizability component parallel to the major axis of the laser polarization [12]. By combining an electrostatic field with an elliptically polarized laser field, three-dimensional potential wells should be produced with the asymmetry along the electrostatic field direction. Thus, three-dimensional molecular orientation is expected to be realized.

Molecular orientation can be enhanced by increasing the laser intensity or the electrostatic field or by lowering the initial rotational temperature [13]. Higher laser intensity forms deeper potential wells and is capable of confining higher rotational states. This increases the number of tunneling doublets involved in the pseudo-first-order Stark effect. On the other hand, increasing the electrostatic field creates a larger anisotropy in the potential. When the initial rotational temperature is lowered, the population of high rotational states in the initial sample decreases. All of these contribute to the enhancement of molecular orientation.

We observed three-dimensional molecular orientation with our novel technique in which two-dimensional ion imaging and time-of-flight (TOF) mass spectrometry are complementarily used. The schematic diagrams of the two modes of observations are shown in Fig. 1. Three-dimensional alignment can be confirmed with two-dimensional ion imaging technique [12]. Orientation is verified by analyzing TOF spectra [13]. The two kinds of

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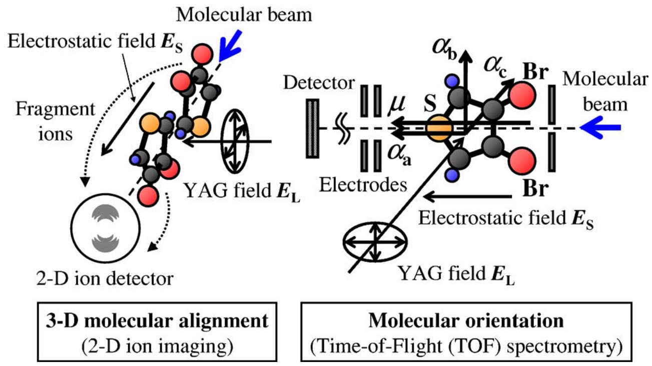

FIG. 1. (Color online) Schematic diagrams of the two observations made. Three-dimensional alignment is confirmed with the two-dimensional ion imaging technique (on the left) and molecular orientation is verified by time-of-flight (TOF) mass spectrometry (on the right). μ and α designate the permanent dipole moment and the polarizability of 3,4-dibromothiophene molecule [18], respectively.

observations can be made using the same apparatus.

In order to demonstrate three-dimensional orientation, we need a molecule with a nonzero permanent dipole moment and three different components of the molecular polarizability. As a sample molecule, we used 3,4-dibromothiophene (DBT) illustrated in Fig. 1 [18]. We focus on the ions from the Br and S atoms for observing the effect of three-dimensional orientation.

In order to achieve molecular orientation, we irradiate the sample molecules with an intense nanosecond laser pulse [Nd:YAG (yttrium aluminum garnet), ~12 ns, $\sim 10^{12}$ W/cm^2]. The duration of the YAG pulse is sufficiently longer than the rotational period of DBT (on the order of 100 ps), and molecular orientation proceeds in the adiabatic regime [19]. For the purpose of probing molecular orientation, a femtosecond probe pulse (Ti:sapphire, ~50 fs, $\sim 10^{15}$ W/cm^2) is used to multiply ionize the molecules at the peak of the YAG pulse when the highest degree of orientation should be achieved [10]. The multiply ionized molecules dissociate into fragment ions, which are detected by the microchannel plate (MCP) either as ion images or as TOF spectra to confirm three-dimensional orientation. The two collinear laser beams are focused at the intersection with a pulsed molecular beam, or the "interaction point." The focal spot radius of the probe pulse (~14 μm) is adjusted to be smaller than that of the YAG pulse (~24 μm), ensuring that we probe the portion with the highest intensity of the YAG pulse. The molecular beam is formed by expanding DBT molecules seeded in He gas into a vacuum chamber through the 0.5-mm-diam nozzle of a pulse valve. The partial pressure of DBT is 7 Torr, and the total pressure of the sample gas (the backing pressure) is varied from 1 to 8 atm. The vacuum chamber is separated into two parts with two skimmers and is differentially pumped. The high-vacuum side of the chamber serves as a TOF mass spectrometer and two-dimensional ion imaging apparatus. The background pressure of the high-vacuum side is $\sim 10^{-8}$ Torr in operation. The interaction point is located at the middle point between the repeller and extractor of the TOF spectrometer. We use the acceleration field of the TOF spectrometer also as an electrostatic field for molecular orientation [13]. Thus, at the interaction point, rotationally cold molecules are exposed to both an electrostatic field and an intense, elliptically polarized laser field.

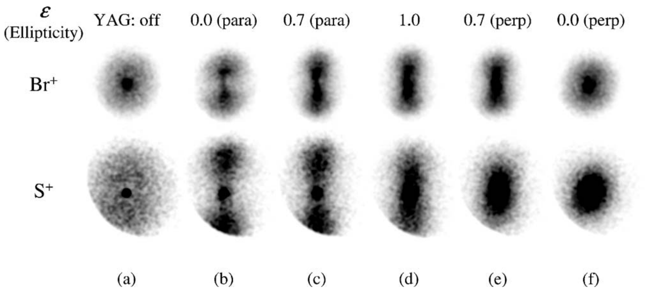

FIG. 2. Ion images of Br$^+$ (top row) and S$^+$ (bottom row) fragments obtained with different ellipticities of the YAG pulse (3×10^{12} W/cm^2). The labels "(para)" and "(perp)" show the major axis of the polarization *parallel* and *perpendicular* to the detector plane, respectively.

First, we verify three-dimensional molecular alignment with an elliptically polarized laser field using the ion imaging technique. The acceleration field of the TOF spectrometer is adjusted for velocity mapping so that the fragments with the same initial velocity arrive at the same position on the detector [20]. Figure 2 shows the ion images of Br$^+$ and S$^+$ ions observed with various ellipticities of the YAG pulse. Ellipticity is defined as $\varepsilon = E_{\mathrm{min}}/E_{\mathrm{maj}}$, where E_{maj} and E_{min} are the major and minor axis components of the laser electric field, respectively. In a similar observation by Larsen *et al.*, only a quarter-wave plate is used to change the ellipticity of the YAG pulse and the polarization axes are rotated when the ellipticity is changed [12]. A more appropriate way to change the ellipticity is to rotate a half-wave plate placed before a fixed quarter-wave plate. This method enables us to use an arbitrary ellipticity while keeping the directions of the two axes of the ellipse fixed in the laboratory frame. The labels "(para)" and "(perp)" in Fig. 2 show the major axis of the polarization *parallel* and *perpendicular* to the detector plane, respectively. Here, the probe pulse is circularly polarized in order to avoid the effects of enhanced ionization [21].

Ion images in Fig. 2(a) are obtained without the YAG pulses. They look almost isotropic, indicating that the molecules are randomly directed. When we apply the YAG pulses (3×10^{12} W/cm^2), an anisotropy is observed [Figs. 2(b)–2(f)]. When the YAG pulses are linearly polarized with their polarization *parallel* to the detector plane [Fig. 2(b)], both Br$^+$ and S$^+$ ions are gathered along the polarization direction and are separated into top and bottom portions. Considering the structure of DBT (Fig. 1), we can interpret Fig. 2(b) as evidence that the major axis of the molecule (defined as the axis with the largest polarizability) is confined parallel to the polarization direction. Figure 2(f), obtained with linear polarization *perpendicular* to the detector plane, complements Fig. 2(b) with isotropic images showing a cylindrically symmetric distribution of both Br$^+$ and S$^+$ around the laser polarization. When the polarization is circular [Fig. 2(d)], the fragment ions are confined along the ver-

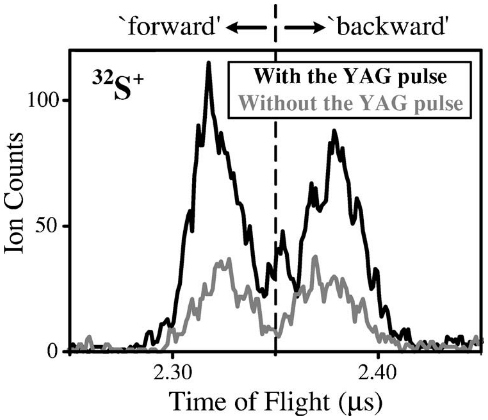

FIG. 3. The peaks of S^+ ions in the TOF spectra obtained with (black) and without (gray) the YAG pulse (3×10^{12} W/cm^2). The electrostatic field and the backing pressure are 760 V/cm and 8 atm, respectively.

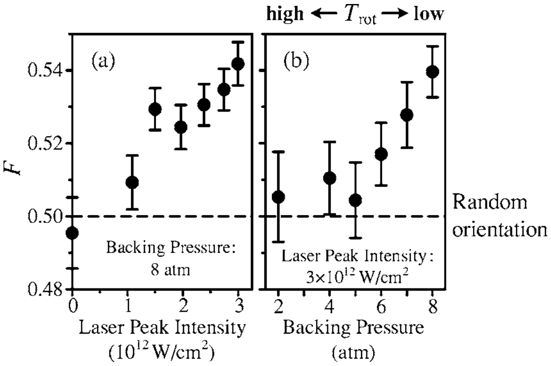

FIG. 4. The dependence of the value F (defined in the text) for S^+ on (a) the peak intensity of the YAG pulse and (b) the backing pressure of the sample gas. T_{rot} is the rotational temperature of the sample gas. The electrostatic field is 760 V/cm in both cases.

tical direction, but the separation into top and bottom parts is not observed as in Fig. 2(b). This is consistent with the theoretical prediction that the molecular plane becomes confined to the plane of the circular polarization, but the molecule is free to rotate in the polarization plane [12]. Figures 2(c) and 2(e) are obtained with an elliptical polarization ($\varepsilon=0.7$) with the major axis of the ellipse *parallel* and *perpendicular*, respectively, to the detector plane. In both images, Br^+ fragments are confined along the vertical direction. When Fig. 2(e) is compared to Fig. 2(f), the effect of elliptical polarization is prominent in extending the image of Br^+ in the vertical direction and compressing in the horizontal direction. These observations show that the molecules are confined parallel to the elliptical polarization plane. In addition, the images of S^+ fragments in Figs. 2(c) and 2(e) indicate that the major axes of the molecules are confined parallel to that of the elliptical polarization. The images in Fig. 2 clearly show that, under the presence of an elliptically polarized laser field, the molecules are confined in the polarization plane with their major axes parallel to the major axis of the laser polarization. These observations are consistent with the demonstration of three-dimensional alignment by Larsen *et al.* [12] and the employment of the complementary configurations for the major axis of laser polarization and the proper procedure for changing the ellipticity makes our observations more reliable.

Next, we examine the "head-versus-tail" direction of the molecules when an electrostatic field is also present. For this observation, we make the major axis of the YAG laser polarization perpendicular to the detector plane—i.e., parallel to the TOF axis. Here, we use linear polarization to utilize the highest available laser electric field in the direction of the major axis under the present condition [22]. As mentioned previously, the acceleration field (760 V/cm) of the TOF mass spectrometer serves also as an electrostatic field to orient the molecules. The probe pulse is linearly polarized parallel to the TOF axis. Under this configuration, we compare the peaks of S^+ ions in TOF spectra (Fig. 3) obtained with (black) and without (gray) the YAG pulse (3×10^{12} W/cm^2). The backing pressure is 8 atm. There are two peaks in each spectrum. The peak at earlier time consists of "forward" fragments which are emitted toward the detector during the dissociative ionization. The other peak at later time is composed of "backward" fragments which are initially emitted away from the detector. Considering the direction of the permanent dipole moment of DBT as illustrated in Fig. 1, the S atom of DBT should be directed toward the detector if orientation is achieved in the present setup, thus increasing the forward S^+ fragments. In the spectrum obtained without the YAG pulse the two peaks are almost symmetric, indicating random orientation. This confirms that the effect of nonadiabatic orientation [19] caused by the intense femtosecond probe pulse is negligible in this experiment. On the other hand, we can observe a noticeable asymmetry when the YAG pulse is applied. The intensity of the forward peak is more enhanced than that of the backward peak, which indicates that more than half the molecules are oriented with the S atoms directed toward the detector. This observation agrees with our expectation and can be considered as the evidence of molecular orientation.

We introduce the value $F\equiv I_{\mathrm{f}}/(I_{\mathrm{f}}+I_{\mathrm{b}})$ as a measure of the degree of orientation. Here I_{f} and I_{b} are the integrated signals of the forward and backward fragments, respectively. When the molecules are randomly oriented or only aligned, $F=0.5$. In the case of DBT, a larger value of F for S^+ ions means a higher degree of orientation.

We observe the dependence of F for S^+ on the three parameters predicted to affect the degree of orientation: namely, the peak intensity of the YAG pulse, the electrostatic field strength, and the rotational temperature. The rotational temperature can be lowered by increasing the backing pressure [23]. The results are summarized in Fig. 4. Unfortunately, a notable change in F cannot be observed when the electrostatic field strength is varied because of the small variable range with the present experimental setup (note that the electrostatic field has to be always applied in order to serve as the acceleration field of the TOF mass spectrometer). It can be seen that F increases when the laser intensity is increased with the backing pressure held constant at 8 atm [Fig. 4(a)] and when the backing pressure is increased with the intensity of the YAG pulse constant at 3×10^{12} W/cm^2 [Fig. 4(b)]. In both cases the electrostatic field is 760 V/cm and the highest value of *F* obtained is 0.54. Both results in Fig. 4 are consistent with our expectations that orientation is enhanced as the laser intensity is increased or as the rotational temperature is lowered. In addition to the observation in Fig. 3, the results shown in Fig. 4 provide us with stronger evidence of orientation of DBT molecules with the S atoms directed toward the detector.

For the present experiment, we confirm molecular orientation by analyzing the TOF spectra and evaluate the degree of orientation in terms of the value *F*. Direct observation of the angular distribution of fragment ions is included in future subjects. One of the possible methods to achieve this is to use a three-dimensional ion detection method [24].

Another step in molecular manipulation is the experimental achievement of nonadiabatic molecular orientation [19]. Nonadiabatic alignment has been established in the past few years [25] and has already been used for some interesting applications [4]. Nonadiabatic molecular orientation will provide us with another useful system in which an oriented sample can be prepared in an environment where the intense laser field is absent.

In conclusion, by observing ion images in an appropriate manner, three-dimensional alignment is reconfirmed to be feasible using an elliptically polarized laser field. On the other hand, TOF spectra show that, when an electrostatic field is present together with the laser field, DBT molecules are oriented with the S atoms directed toward the detector. These results from the two complementary experiments give us firm evidence that we have achieved three-dimensional molecular orientation for the first time to our knowledge. This is a clear advance in the course of molecular manipulation studies based on laser technologies.

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

[2] “Alignment” refers to a state where the molecular axes are parallel to each other but no attention is paid to the “head-versus-tail” directions. “Orientation” designates a state where not only are the axes parallel but also the heads of the molecules are directed the same way.

[3] T. Suzuki, S. Minemoto, T. Kanai, and H. Sakai, Phys. Rev. Lett. **92**, 133005 (2004).

[4] T. Kanai, S. Minemoto, and H. Sakai, Nature (London) **435**, 470 (2005).

[5] Special issue on *Stereodynamics of Chemical Reaction* [J. Phys. Chem. A **101**, 7461 (1997)].

[6] C. H. Parker and R. B. Bernstein, Annu. Rev. Phys. Chem. **40**, 561 (1989).

[7] B. Friedrich and D. Herschbach, Nature (London) **353**, 412 (1991).

[8] B. Friedrich and D. Herschbach, Phys. Rev. Lett. **74**, 4623 (1995).

[9] B. Friedrich and D. Herschbach, J. Phys. Chem. A **103**, 10280 (1999).

[10] H. Sakai *et al.*, J. Chem. Phys. **110**, 10235 (1999).

[11] J. J. Larsen *et al.*, J. Chem. Phys. **111**, 7774 (1999).

[12] J. J. Larsen, K. Hald, N. Bjerre, H. Stapelfeldt, and T. Seideman, Phys. Rev. Lett. **85**, 2470 (2000).

[13] H. Sakai, S. Minemoto, H. Nanjo, H. Tanji, and T. Suzuki, Phys. Rev. Lett. **90**, 083001 (2003); S. Minemoto *et al.*, J. Chem. Phys. **118**, 4052 (2003).

[14] R. A. Bartels *et al.*, Opt. Lett. **28**, 346 (2003).

[15] T. Seideman, J. Chem. Phys. **107**, 10420 (1997).

[16] W. Kim and P. M. Felker, J. Chem. Phys. **104**, 10420 (1996).

[17] G. R. Kumar, P. Gross, C. P. Safvan, F. A. Rajgara, and D. Mathur, Phys. Rev. A **53**, 3098 (1996).

[18] $\mu = 1.59$ D [26], $\alpha_a = 20.6$ Å^3, $\alpha_b = 16.0$ Å^3, and $\alpha_c = 10.1$ Å^3 [12].

[19] L. Cai, J. Marango, and B. Friedrich, Phys. Rev. Lett. **86**, 775 (2001).

[20] A. T. J. B. Eppink and D. H. Parker, Rev. Sci. Instrum. **68**, 3477 (1997).

[21] E. Constant, H. Stapelfeldt, and P. B. Corkum, Phys. Rev. Lett. **76**, 4140 (1996).

[22] We recently confirmed that one-dimentional molecular orientation can be achieved with elliptical polarization using OCS molecules as a sample. Since the principle of three-dimentional molecular orientation is based on the combination of three-dimentional alignment and one-dimentional orientation, the results presented here together with our recent observation ensure that the three-dimentional molecular orientation of DBT molecules has been actually achieved, for example, under the condition shown in Fig. 2(e).

[23] The rotational temperature of DBT molecules is estimated to be well below 5 K at the backing pressure of 8 atm [27].

[24] R. Dörner *et al.*, J. Phys. B **28**, 435 (1995).

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

[26] T. Shimozawa, Bull. Chem. Soc. Jpn. **38**, 1046 (1965).

[27] *Atomic and Molecular Beam Methods*, edited by G. Scoles (Oxford University Press, New York, 1988), Vol. 1.