

## Laser-field-free orientation of state-selected asymmetric top molecules

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With combined electrostatic and shaped laser fields with a slow turn on and rapid turn off, laser-field-free orientation of asymmetric top iodobenzene molecules with higher degrees of orientation has been achieved. In order to further increase the degrees of orientation, state-selected molecules are used as a sample. It is confirmed that higher degrees of orientation are maintained in the laser-field-free condition for 5–10 ps, which is long enough to study femtosecond-attosecond dynamics in molecules, after the rapid turn off of the laser pulse. The observation of the slow dephasing time of 5–10 ps ensures future prospects in molecular orientation techniques. This accomplishment means not only that a unique molecular sample has become available in various applications but also that the present technique can be used as a spectroscopic technique to investigate ultrafast rotational dynamics of molecules.

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The laser-based techniques of molecular alignment and orientation have progressed remarkably since the pioneering works reporting the first experimental demonstration of adiabatic molecular alignment with an intense nonresonant laser field [1,2]. Molecular alignment techniques are well established and used in many applications [3].

In recent years, it is clear that the attention of researchers is turning to the development of various molecular orientation techniques, which is evidenced by the rapid progress in these techniques. Based on the theoretical proposal by Friedrich and Herschbach [4,5], our group has demonstrated both one- [6,7] and three-dimensional orientation [8] of ordinary molecules with a linearly and elliptically polarized laser field, respectively, in the presence of a weak electrostatic field. After that, laser-field-free molecular orientation with combined electrostatic and rapidly turned-off laser fields was proposed [9], and demonstrated [10] by rapidly turning off a nanosecond laser pulse at its peak intensity with the plasma shutter technique. In 2009, by using a sample of state-selected  $C_6H_5I$  molecules prepared with a molecular deflector, higher degrees of orientation are reported in the adiabatic regime [11], whereas by using a sample of state-selected NO molecules prepared by a hexapole focuser, higher degrees of orientation are reported in the nonadiabatic regime [12]. On the other hand, all-optical molecular orientation with an intense nonresonant two-color laser field was proposed [13], and demonstrated [14]. In Ref. [15], it is reported that laser-field-free orientation of CO molecules is observed with intense femtosecond two-color laser pulses. More recently, it is demonstrated that carbonyl sulfide (OCS) molecules are oriented by intense single-cycle THz pulses [16]. The research and development of molecular orientation techniques is becoming more and more active.

With all available techniques associated with the combined-field technique at the present stage successfully combined, here we demonstrate laser-field-free orientation of state-selected asymmetric top molecules with higher degrees of orientation. (1) In order to achieve higher degrees of orientation, rotationally cold molecules are prepared as an initial sample

as described below [17]. In order to achieve even higher degrees of orientation, molecules in lower-lying rotational states are selected by deflecting a molecular beam with a molecular deflector [11]. (2) Since rotational states are closely distributed in their energies of asymmetric top molecules, it is virtually impossible to prepare a single rotational state even with a molecular deflector. For those molecules not in a single rotational state but in some lower-lying rotational states, some of which are oriented one way and the others are oriented the other way, it is of crucial importance to create molecular orientation adiabatically so that the rotational states in the molecules can tunnel from the shallower potential well to the deeper one and the highest possible degrees of orientation can be achieved [9,18]. (3) In order to achieve laser-field-free orientation, the pump laser pulse is rapidly turned off at its peak intensity by the plasma shutter technique as proposed by us [9]. Then the laser-field-free molecular orientation is realized just after the rapid turn off of the pump pulse.

The sample is  $C_6H_5I$  (iodobenzene) molecules buffered with 60 bars He and supplied as a supersonic molecular beam by an Even-Lavie valve [19]. The molecular beam passes through a 3-mm-diam skimmer and enters the molecular deflector. The molecular deflector is homebuilt by reference to Refs. [11,20]. Then the (un)deflected molecules enter the interaction region and are crossed at right angles by the pump and probe pulses. As a pump pulse, the fundamental pulse from an injection-seeded single-longitudinal-mode Nd:YAG laser (Spectra-Physics, LAB-130-10) with the pulse width of 12 ns is used. As a probe pulse, an output from a Ti:sapphire-based chirped pulse amplification system (Spectra-Physics, Spitfire Ace 35F) with the center wavelength of 800 nm and the pulse width of 35 fs is used. A part of the output from the Ti:sapphire amplifier is also used as a trigger pulse of the plasma shutter. The pump and probe pulses are collinearly focused by a 300-mm-focal-length lens onto the molecular beam. Instantaneous spatial orientation of the sample molecules is observed by Coulomb exploding the molecules with the probe pulse in the velocity-map imaging spectrometer. The produced  $I^+$  fragment ions are detected by a microchannel plate backed by a phosphor screen. The ion images on the phosphor screen are recorded by a charge-coupled device camera.

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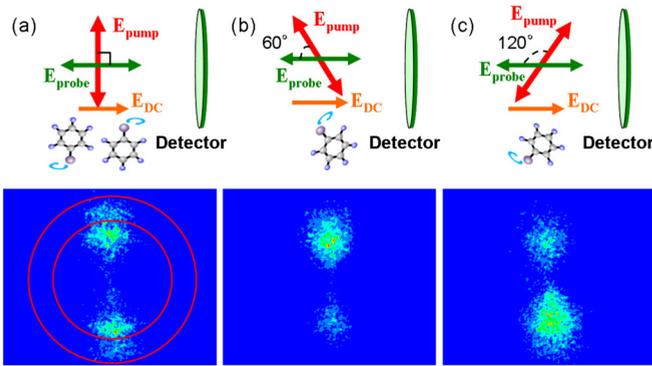


FIG. 1. (Color online) The observations of molecular alignment and orientation. (a) When observing alignment, the polarizations of the pump and probe pulses are parallel and perpendicular to the detector plane, respectively. (b) and (c) When observing orientation, the polarization of the pump pulse is tilted  $60^\circ$  or  $120^\circ$  from the time-of-flight axis to utilize the combined effect of the electrostatic and the pump laser fields, whereas the probe polarization is perpendicular to the detector plane. In (a)–(c), also included are the ion images for molecular alignment and orientation observed with a sample of state-selected molecules. See the text for the details.

As shown in Fig. 1(a), when we observe molecular alignment, the polarizations of the pump and probe pulses are set parallel and perpendicular to the detector plane. The degree of alignment is evaluated by  $\langle \cos^2 \theta_{2D} \rangle$ , where  $\theta_{2D}$  is the polar angle between the pump pulse polarization and the molecular axis projected onto the detector plane. When evaluating  $\langle \cos^2 \theta_{2D} \rangle$ , the  $I^+$  ions observed between the concentric rings in Fig. 1(a), which originate from the Coulomb explosion process  $C_6H_5I + N\hbar\omega \rightarrow C_6H_5I^3+ \rightarrow C_6H_5^{2+} + I^+$ , are used [2,11].

As shown in Figs. 1(b) and 1(c), when we observe molecular orientation, the polarization of the pump pulse is tilted  $60^\circ$  or  $120^\circ$  to utilize the combined effect of the electrostatic and the pump laser fields, whereas the probe polarization remains perpendicular to the detector plane. Throughout the present study, the electrostatic field, which is originally the acceleration field of the velocity-map imaging spectrometer, is  $2.4 \text{ kV/cm}$ . The degree of orientation is characterized by the ratio  $N_{\text{up}}/N_{\text{total}}$ , where  $N_{\text{up}}$  is the number of the fragment ions observed in the upper half of the ion image and  $N_{\text{total}}$  is the total number of the fragment ions observed in the ion image [11]. When the polarization of the pump pulse is tilted, the double-ring structure in the ion images gets blurred. We therefore employ all the  $I^+$  ions in the images to evaluate  $N_{\text{up}}/N_{\text{total}}$ .

We first measure the vertical intensity profile of the  $C_6H_5I$  molecular beam with the applied voltages of 0 and 5 kV to the molecular deflector. Since the lower-lying rotational states of  $C_6H_5I$  molecules are all high-field seekers, it is expectedly confirmed that the molecules are actually deflected (upward in our setup) when the applied voltage is 5 kV. When the state-selected molecules are used as a sample in the present measurements, we set the focusing position at the  $1/8$  intensity of the peak of the deflected intensity profile obtained with the applied voltage of 5 kV. Figure 1(a) includes the ion image for the molecular alignment observed with a sample of thus state-selected molecules, for which the highest degree of

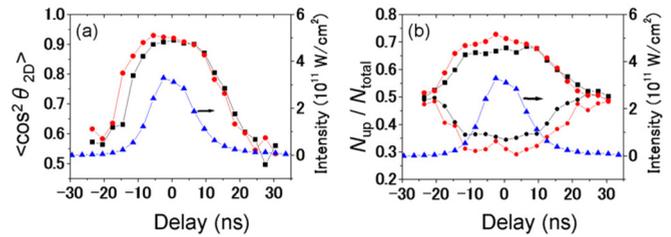


FIG. 2. (Color online) The temporal evolutions of the degrees of alignment (a) and orientation (b) for the thermal ensemble (black squares) and the state-selected molecules (red circles) during the pump pulse (blue triangles) with the peak intensity of  $3.3 \times 10^{11} \text{ W/cm}^2$ .

alignment ( $\langle \cos^2 \theta_{2D} \rangle = 0.91$ ) in the present study is obtained at the peak intensity of the pump pulse of  $3.3 \times 10^{11} \text{ W/cm}^2$ . One can see that the molecules are well aligned with the C-I axis aligned along the polarization of the pump pulse. On the other hand, Figs. 1(b) and 1(c) include the ion images for the molecular orientation observed with a sample of thus state-selected molecules, for which the highest degrees of orientation [ $N_{\text{up}}/N_{\text{total}} = 0.68(0.32)$ ] in the present study are obtained at the same peak intensity of the pump pulse. Since the permanent dipole moment of a  $C_6H_5I$  molecule points from the I atom to the phenyl group [11], one can confirm that the molecules are oriented as expected. When the thermal ensemble is used as a sample, we set the focusing position at the peak of the undeflected intensity profile obtained with the applied voltage of 0 kV.

As pointed out in the introductory part, in order to achieve the highest possible degrees of orientation, it is of crucial importance that the laser-molecule interaction proceeds as adiabatically as possible. If the process is purely adiabatic, it is expected that the degree of orientation follows the temporal evolution of the pump pulse [1,21]. We therefore observe how well the degrees of alignment and orientation follow the temporal evolution of the pump pulse. Figure 2 shows the temporal evolutions of the degrees of alignment (a) and orientation (b) for the thermal ensemble and the state-selected molecules during the pump pulse with the peak intensity of  $3.3 \times 10^{11} \text{ W/cm}^2$ . Seemingly, they closely follow the temporal profile of the pump pulse, suggesting that the laser-molecule interaction proceeds at least in the nearly adiabatic regime. However, here we employ an approach to carefully examine the temporal evolutions of the degrees of alignment and orientation, and to judge how well the laser-molecule interaction proceeds adiabatically. That is, we plot the degrees of alignment and orientation as a function of the instantaneous intensity of the pump pulse on its rising part and falling part, separately. If there is a significant difference between the instantaneous intensity dependence of the degrees of alignment and orientation on the rising part and that on the falling part, it can be used as a measure of the deviation from the adiabatic process.

Although the details of our observations will be presented elsewhere, our observations can be summarized as follows: (1) During the 12-ns pump pulse with the peak intensity of  $3.3 \times 10^{11} \text{ W/cm}^2$ , molecular orientation proceeds not in the purely adiabatic regime but in the nearly adiabatic regime. (2) The different behaviors in the instantaneous intensity

dependence observed between alignment and orientation with the thermal ensemble indicate the necessity of a longer pulse (rise time) to ensure the adiabatic process of molecular orientation [9,18]. (3) The more distinct difference in the instantaneous intensity dependence observed with the state-selected molecules than with the thermal ensemble further suggests the necessity of an even longer pulse (rise time) to ensure the adiabatic process of orientation of the state-selected molecules. This may be explained by the general tendency that lower-lying rotational states take the highest degrees of orientation at lower intensities when the duration (rise time) of the pump pulse is deficiently long. (4) With lower pump pulse intensities (lower than  $\sim 1.0 \times 10^{11} \text{ W/cm}^2$ ), it is experimentally confirmed that there is no clear difference between the instantaneous intensity dependence of the degrees of alignment and orientation on the rising part and that on the falling part within experimental uncertainties, apparently suggesting that the laser-molecule interaction proceeds almost adiabatically. We still note that the apparent agreement between them is a necessary condition, but is not necessarily a sufficient condition to ensure that the laser-molecule interaction is adiabatic.

Then, in order to achieve laser-field-free alignment [22,23] and orientation [9,10] of (state-selected) asymmetric top molecules, we apply the plasma shutter technique. A cross-correlation measurement confirms that the fall time of the pump pulse is about 150 fs. Here we focus on the temporal evolutions of alignment and orientation just after the rapid turn off of the pump pulse, which is also motivated by the fact that laser-field-free three-dimensional alignment and orientation can be expected only just after the rapid turn off of the pump pulse.

We first look at the temporal evolutions of alignment. Figure 3 shows the temporal evolutions of alignment of the thermal ensemble (a) and the state-selected molecules (b) observed with the two intensities of  $1.7 \times 10^{11} \text{ W/cm}^2$  and  $6.0 \times 10^{10} \text{ W/cm}^2$ . Before the rapid turn off of the pump

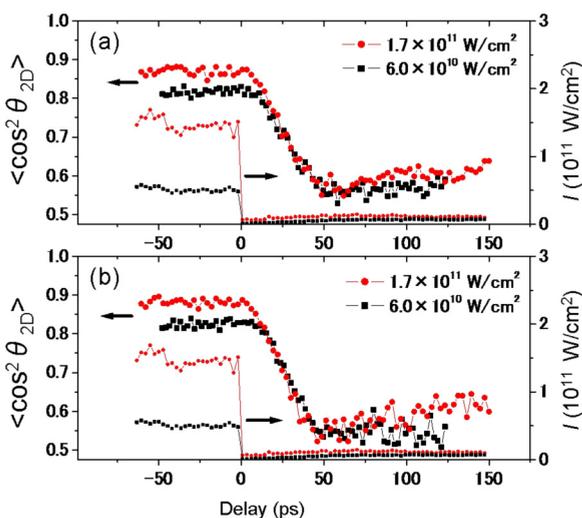


FIG. 3. (Color online) The temporal evolutions of alignment of the thermal ensemble (a) and the state-selected molecules (b) observed with the two intensities of  $1.7 \times 10^{11} \text{ W/cm}^2$  and  $6.0 \times 10^{10} \text{ W/cm}^2$ , for which the temporal profiles of the shaped pump pulses are also included.

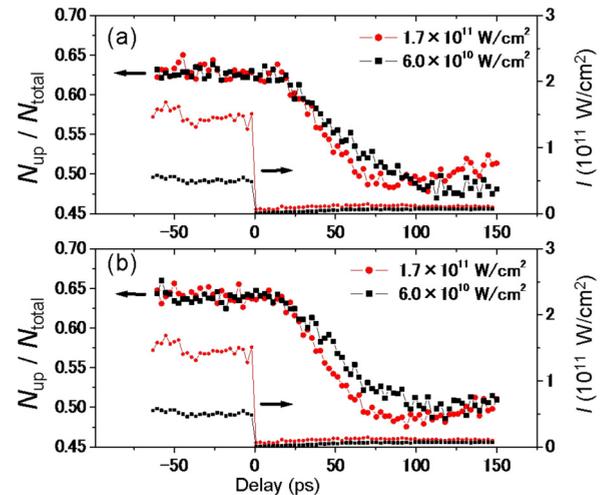


FIG. 4. (Color online) The same as in Fig. 3 but for orientation.

pulse, the degrees of alignment are higher at  $1.7 \times 10^{11} \text{ W/cm}^2$  than at  $6.0 \times 10^{10} \text{ W/cm}^2$ . After the rapid turn off of the pump pulse, one can see that higher degrees of alignment are maintained in the laser-field-free condition for 5–10 ps, which is long enough for various applications on electronic stereodynamics in molecules with femtosecond pulses [24]. In addition, it is confirmed that the dephasing is more rapid with  $1.7 \times 10^{11} \text{ W/cm}^2$  than with  $6.0 \times 10^{10} \text{ W/cm}^2$ , which is more distinct for the state-selected molecules than for the thermal ensemble. The more rapid dephasing with higher intensities of the pump pulse is understood by considering that higher rotational states are excited with higher intensities of the pump pulse and the rotational motions of the higher excited rotational states are more rapid, resulting in the more serious interferences among the molecules in different rotational states and leading to the more rapid dephasing.

Figure 4 shows the temporal evolutions of orientation of the thermal ensemble (a) and the state-selected molecules (b) observed with the two intensities of  $1.7 \times 10^{11} \text{ W/cm}^2$  and  $6.0 \times 10^{10} \text{ W/cm}^2$ . Before the rapid turn off of the pump pulse, the degrees of orientation are almost the same for the two intensities, which reflects the strong saturation tendency of orientation as can be seen in Fig. 2(b). After the rapid turn off of the pump pulse, one can see that higher degrees of orientation are maintained in the laser-field-free condition for  $\sim 20$  ps, which is apparently longer than the duration, during which higher degrees of alignment are maintained. However, the apparently longer duration of orientation comes from the employed measure of orientation  $N_{up}/N_{total}$ , and the actual duration of orientation when evaluated in terms of commonly used  $\langle \cos^2 \theta_{2D} \rangle$  should be reasonably considered to be slightly longer than that of alignment, i.e., 5–10 ps [10]. As in the case of alignment, it is also confirmed that the dephasing is more rapid with  $1.7 \times 10^{11} \text{ W/cm}^2$  than with  $6.0 \times 10^{10} \text{ W/cm}^2$ , which is again more distinct for the state-selected molecules than for the thermal ensemble.

We note that the dephasing dynamics of both alignment and orientation is very slow compared to that observed for the OCS molecules reported in Ref. [10]. First we confirm that the

slow dephasing of alignment and orientation is *not* due to the residual component of the rapidly turned-off pump pulse. As has been described in Ref. [10], the residual component of the switched pulse is 5% in intensity. However, it should be noted that the residual component of 5% is the result of the cross-correlation measurement. Our numerical simulations confirm that good agreements between the observations and the calculations shown in Figs. 3 and 4 of Ref. [10] ensure that the residual laser field component must be smaller than 10 kV/cm [25], which is as low as four times the electrostatic field (2.4 kV/cm) used in the present experiment. This means that the effect of the residual component to the dephasing dynamics of both alignment and orientation is virtually negligible. Therefore, it is justified to say that we have achieved laser-field-free alignment and orientation of state-selected asymmetric top molecules.

It seems to be reasonable to think that the slow dephasing of both alignment and orientation is a phenomenon that characterizes asymmetric top molecules such as an iodobenzene molecule after the complete turn off of the 6-ns quasiadiabatic pulse with lower intensities of  $\sim 10^{11}$  W/cm<sup>2</sup>. In general, the dynamics of both alignment and orientation after the rapid turn off of the pump pulse should depend on how the sample molecules are rotationally excited on the rising part of the pump pulse, i.e., the specific combination of excitation parameters such as both an intensity and a duration (rising time) of the pump pulse, the magnitude of the electrostatic field, the molecular constants, and the rotational state distributions in the sample molecules [26]. This means that choosing an optimal combination of excitation parameters gives us a very important possibility of controlling the dynamics of both alignment and orientation after the rapid turn off of the pump pulse. We believe that the laser-molecule interaction's deviation from the adiabatic limit may play a key role in the observed very slow dephasing of both alignment and orientation. In addition, we have found that the dephasing dynamics after the rapid turn off of the pump pulse actually depends on the intensity of the pump pulse. Since the dephasing dynamics gives us information about how Majorana transitions among the rotational quantum states in the molecules proceed, our experimental technique presented here (nanosecond pump followed by femtosecond dump) can be a molecular spectroscopic technique to investigate ultrafast Majorana transitions in molecules which cannot be investigated with other existing spectroscopic techniques.

The observation of the slow dephasing time of 5–10 ps ensures future prospects in molecular orientation techniques. By using elliptical polarization instead of linear polarization in the combined-field technique, laser-field-free three-dimensional orientation will be achieved [8–10] and its implementation is now in progress in our laboratory. On the other hand, we have recently demonstrated all-optical molecular orientation with an intense nonresonant two-color laser field in the adiabatic regime [13,14]. By using the state-selected molecules as a sample and by applying the plasma shutter technique, *completely field-free molecular orientation* with higher degrees of orientation will be achieved just after the rapid turn off of the pump pulse [27]. With the polarizations of two-color laser fields parallel to each other, molecular orientation will be one-dimensionally controlled, whereas with the two polarizations crossed, molecular orientation will be three-dimensionally controlled [14,28]. Since we have all the necessary experimental techniques to develop these unexplored molecular orientation techniques, they will also be implemented in our group in the near future.

In summary, we have demonstrated laser-field-free orientation of state-selected asymmetric top molecules. This is a clear advance in the course of the development of various techniques on molecular orientation and ensures future prospects as discussed above. It is emphasized that because the laser-molecule interaction relies on the nonresonant process, the present technique is versatile and can be applied to any (asymmetric top) molecule both with a moderate permanent dipole moment and with a moderate polarizability anisotropy.

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