Controlling the Orientation of Polar Molecules with Combined Electrostatic and Pulsed, Nonresonant Laser Fields

Hirofumi Sakai,* Shinichirou Minemoto, Hiroshi Nanjo, Haruka Tanji, and Takayuki Suzuki
Department of Physics, Graduate School of Science, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

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We demonstrate that molecules with a moderate permanent dipole moment can be oriented with combined electrostatic and pulsed, nonresonant laser fields. We use OCS molecules as a sample. The degree of orientation can be increased by increasing the magnitude of electrostatic field and the peak intensity of the laser field or by decreasing the rotational temperature of the molecules.

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The manipulation of atoms and molecules is one of the most important and intriguing subjects in modern physics, chemistry, and biology. The control of the spatial direction of molecules is especially important for studies of orientational effect in chemical reaction dynamics [1]. The alignment of neutral molecules by a strong linearly polarized laser field has already been demonstrated [2,3]. At present, strong electrostatic field orientation and electric hexapole focusing are used to control the orientation of polar molecules. However, strong electrostatic field orientation is effective only for certain molecules possessing large permanent dipole moments and electric hexapole focusing works only for symmetric top molecules. The experimental realization of molecular orientation to arrange *any* polar molecules in a "head-versus-tail" order is a next challenging subject and should greatly expand the range of applications in stereodynamical studies of chemical reaction dynamics.

So far, several approaches are theoretically proposed to achieve molecular orientation based on laser technologies [4–7]. Recently, Friedrich and Herschbach suggested exploiting combined electrostatic and nonresonant induced dipole forces to enhance the orientation of polar molecules [8,9]. Their approach (hereafter the FH method) is based on the combined effect of both the anisotropic polarizability interaction of the induced dipole moment of molecules with an intense nonresonant laser field and the interaction of the permanent dipole moment of the molecules with an electrostatic field. The induced dipole interaction produces a double-well potential. The pendular energy levels form nearly degenerate tunneling doublet states of opposite parity. If the molecule is polar, the introduction of an electrostatic field couples the components of a given tunneling doublet. Thus, even a relatively weak electrostatic field can convert second-order alignment by a laser field into a strong first-order orientation.

Baumfalk *et al.* claim the experimental realization of the FH method for the new molecular species HXeI which has a fairly large permanent dipole moment of 6.4 D [10], though the main purpose of their experiment was the identification of the HXeI molecules in the gas phase using the FH method. However, their observations include some unclear aspects: (i) Although they observed the experimental results suggesting the orientation of the HXeI molecules, they did not observe any effects for other molecules in the series, HKrI and HXeBr, though the values of their orientation cosine are large enough for orientational effects to be observed [11]. (ii) They did not observe any difference when they rotated the laser polarization by 90°. Therefore, it is clear that further investigations are necessary to verify the efficacy of the FH method.

Here we demonstrate clear evidence of orientation of molecules with a moderate permanent dipole moment based on the FH method. In this Letter, we show the results obtained for OCS, which has a permanent dipole moment of 0.71 D [12]. All of our experimental results are consistent with the theoretical expectations as shown below.

The molecular orientation is investigated by a Coulomb explosion experiment using intense femtosecond laser pulses and a time-of-flight (TOF) mass spectrometer. A pulsed supersonic beam of OCS molecules is formed by expanding OCS molecules diluted (5%) with argon (Ar) or helium (He) gas through a 0.25-mm-diam nozzle. The molecular beam is parallel to the TOF axis and crossed at 90° by the focused laser beams. To achieve molecular orientation, we apply fundamentals (wavelength $\lambda = 1064$ nm) from an injection-seeded Nd:YAG (Quanta-Ray, GCR-130) laser and utilize an extraction field of the TOF spectrometer also as an electrostatic field of the FH method. The polarization direction of the YAG (yttrium aluminum garnet) pulse is set to be parallel to the TOF axis to utilize the FH method. The typical pulse width of the YAG pulse is ~12 ns (full width at half-maximum) and the maximum peak intensity used is 2.6×10^{12} W/cm^2. The 12-ns-long pulses ensure that our experiment is performed in an adiabatic regime where the orientation proceeds slowly compared to the rotational period of the molecule. Since we are interested in the orientation of "neutral" molecules, the peak intensity of the YAG pulse is essentially limited by the onset of molecular ionization. In the present experiments, however, it is restricted to a modest level to avoid any damage of optical materials such as a polarizer in the optical path and the window of the TOF spectrometer.

An intense femtosecond laser pulse (hereafter "probe" pulse) is used to ionize the OCS molecules at the peak of the YAG pulse to see the degree of orientation. The electric signals from the controller for the amplified laser system are used to control the timings of the whole experimental system and the YAG pulses are electronically synchronized to the probe pulses with a precision better than ± 0.5 ns. The femtosecond laser pulses come from a Ti-sapphire based amplified laser system (Spectra-Physics, Super Spitfire) and are centered at ~ 800 nm. The typical pulse width is 45 fs and the maximum peak intensity used is 3×10^{14} W/cm^2. The laser pulses are spatially overlapped using a dichroic mirror and focused by a 30-cm-focal-length lens into interaction region of the TOF spectrometer. We carefully adjust the focal spot size of the probe pulse to be smaller than that of the YAG pulse to ensure that we probe only those molecules that have been exposed to the YAG pulse. Actually, the focal spot radii of the YAG and the probe pulses are $\omega_0^{\mathrm{YAG}} \sim 25$ μm and $\omega_0^{\mathrm{probe}} \sim 14$ μm, respectively. The ionized fragments are accelerated by a static electric field toward a microchannel plate (MCP, Galileo, AP TOF-18) detector positioned on-axis with the TOF axis.

When the polarization direction of the probe pulse is parallel to the TOF axis, we usually observe a pair of peaks consisting of so-called "forward" and "backward" fragments whose initial velocities are directed toward and away from the detector, respectively. This is the result of enhanced ionization [13–15] by which molecules initially aligned along the polarization direction are much more likely to undergo multiple ionization. Figure 1 shows the typical TOF spectra obtained (a) with and (b) without YAG pulses. Here we focus on the S^{3+} ion signals [16]. When the YAG pulses are not applied (b), the forward and the backward signals look almost symmetric, indicating that the molecules are randomly oriented. This observation also ensures that the probe pulse does not play any significant role for the orientation of OCS molecules under the present conditions. The orientation process by an intense femtosecond pulse proceeds in the nonadiabatic regime. Numerical study shows that the orientation does not follow the temporal profile of the femtosecond pulse [17]. Still the effect of nonadiabatic interaction can become significant for higher field strength and for lighter molecules [18].

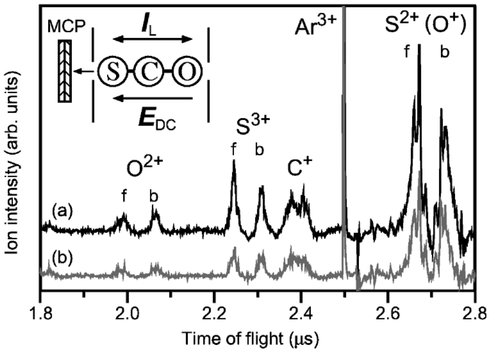

FIG. 1. Typical TOF spectra of OCS molecules (a) with and (b) without Nd:YAG laser pulses. The labels f and b denote fragment ions coming from the "forward" and the "backward" initial emission directions, respectively. The inset shows the directions of the electrostatic field, the linearly polarized laser field, and an oriented OCS molecule.

When we apply the YAG pulses (a), the signals look asymmetric, which we interpret as the result that more than half the OCS molecules are oriented with their S atoms directed toward the detector. This is consistent with our expectation based on a simple consideration about electronegativity. According to the Mulliken's definition using the electron affinity and the ionization potential [12], the electronegativity of the O atom is 7.3 eV and that of the S atom is 6.2 eV. This means that the permanent dipole moment is directed toward the S atom and consequently the molecules tend to be oriented in the way shown in the inset of Fig. 1. The enhancement of the backward signal is the result of the combined effect of molecular alignment and enhanced ionization, i.e., some molecules are not oriented but just aligned. We can confirm our interpretation by observing the change of the signal magnitude of a counterpart fragment, e.g., CO^+. As we expected, the backward signals are larger than the forward signal when we apply the YAG pulses. When we rotate the polarization of the YAG pulse by 90°, the TOF spectrum remains symmetric. This result shows that the combined effect of parallel fields is crucial for the molecular orientation [8,9].

We now move on to the results of quantitative measurements. There are three experimental parameters determining the degree of orientation. They are the peak intensity of the YAG pulse, the magnitude of the electrostatic field, and the backing pressure in the pulsed gas valve (i.e., the rotational temperature of the molecules). We use the quantity of $F = I_f/(I_f + I_b)$ as an order parameter of orientation, where I_f and I_b are the integrated signals of the forward and the backward fragment ions, respectively. When the molecules are randomly oriented or only the molecular alignment is achieved, $F = 0.5$ and if the molecules are completely oriented, F takes the value of 0 or 1.

Figure 2 shows the dependence of the F parameter on the peak intensity of the YAG pulse for the fixed electrostatic field of 380 V/cm. Each data point is the average of 5000 laser shots. The upper panel shows the F parameter of S^{3+} ions from OCS molecules seeded in Ar and the lower panel shows the F parameter of S^{3+} and CO^+ ions from OCS molecules seeded in He. Unfortunately, when Ar is used as a carrier gas, CO^+ ions cannot be observed because of the strong ringing of Ar^{2+} ions. In Ar, the F parameter of S^{3+} ions grows monotonically as the

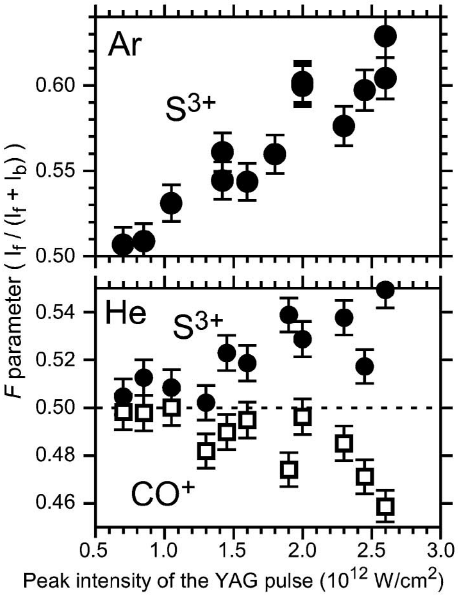

FIG. 2. The dependence of the F parameter (defined in the text) on the peak intensity of the YAG pulse for the fixed electrostatic field of 380 V/cm. The upper panel shows the F parameter of S^{3+} ions from OCS molecules seeded in Ar and the lower panel shows the F parameter of S^{3+} and CO^+ ions from OCS molecules seeded in He. The backing pressure of Ar and He is 8 atm.

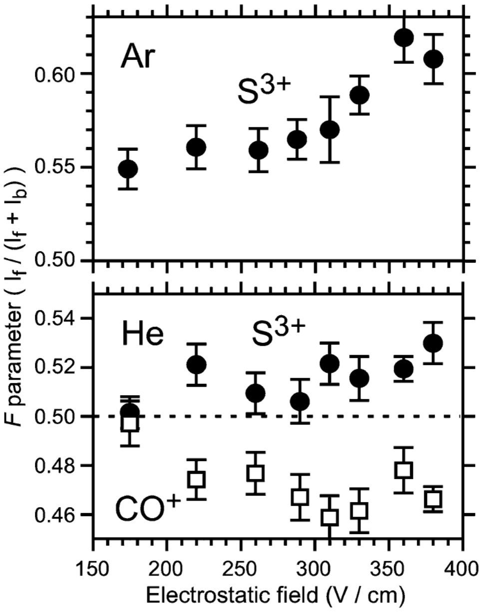

FIG. 3. The dependence of the F parameter (defined in the text) on the electrostatic field for the fixed YAG laser intensity of 2.6×10^{12} W/cm^2. The upper panel shows the F parameter of S^{3+} ions from OCS molecules seeded in Ar and the lower panel shows the F parameter of S^{3+} and CO^+ ions from OCS molecules seeded in He. The backing pressure of Ar and He is 8 atm.

intensity of the YAG pulse is increased and it reaches over 0.60 at 2.6×10^{12} W/cm^2. In He, the F parameter of S^{3+} (CO^+) becomes larger (smaller) for the higher intensity of the YAG pulse and reaches about 0.54 (0.46) at 2.6×10^{12} W/cm^2. The higher degree of orientation observed in Ar than in He is explained by the fact that the rotational temperature of OCS molecules is lower in Ar than in He as discussed below.

Figure 3 shows the dependence of the F parameter on the electrostatic field for the fixed YAG laser intensity of 2.6×10^{12} W/cm^2. Again, the upper panel shows the F parameter of S^{3+} ions from OCS molecules seeded in Ar and the lower panel shows the F parameter of S^{3+} and CO^+ ions from OCS molecules seeded in He. We can see that the overall tendencies are consistent with those observed in Fig. 2.

The rotational temperature of the molecules can be controlled by the carrier gas and/or its backing pressure in the pulsed gas valve. For a fixed backing pressure, the Ar carrier gas can produce a molecular sample with lower rotational temperature than the He carrier gas. For a fixed carrier gas, lower rotational temperature can be achieved by using higher backing pressures. We measure the dependence of the F parameter on the backing pressure in the gas valve for the fixed values of the electrostatic field (380 V/cm) and the YAG laser intensity (2.6×10^{12} W/cm^2). The results are summarized in Fig. 4. In agreement with the FH theory, a higher degree of orientation can be obtained in Ar for a fixed backing pressure and with higher backing pressures for a fixed carrier gas. We observe no sign of space charge effects even with the backing pressure of 8 atm. It is necessary to perform a spectroscopic study to accurately determine the rotational temperature of the molecules under the present conditions.

Although the above measurements are performed separately, the results shown in Figs. 2–4 are consistent with one another, supporting our interpretation that the OCS molecules are oriented. Since the intensity of the YAG pulse and the magnitude of the electrostatic field used in our experiments are still modest, we can further increase the degree of orientation.

We have performed numerical simulations to evaluate the degree of orientation and alignment according to the procedure presented by Friedrich and Herschbach [8,9]. For the electrostatic field of 380 V/cm, the peak laser intensity of 10^{12} W/cm^2, and the rotational temperature of 1 K, we can expect $\langle\langle \cos\theta \rangle\rangle \sim 0.42$ and $\langle\langle \cos^2\theta \rangle\rangle \sim 0.85$ for the degree of orientation and alignment, respectively, where θ is the polar angle between the molecular axis and the direction of the electrostatic field (or the laser polarization in the present case). These significant values are consistent with the fact that we experimentally observe the molecular orientation. A spectroscopic study performed under similar conditions ensures that the rotational temperature lower than 5 K can be achieved under

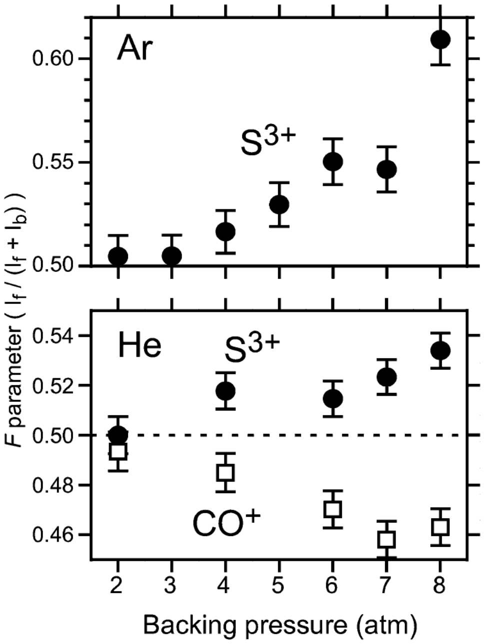

FIG. 4. The dependence of the *F* parameter (defined in the text) on the backing pressure in the gas valve for the fixed values of the electrostatic field (380 V/cm) and the YAG laser intensity (2.6×10^{12} W/cm^2). The upper panel shows the *F* parameter of S^{3+} ions from OCS molecules seeded in Ar and the lower panel shows the *F* parameter of S^{3+} and CO^+ ions from OCS molecules seeded in He.

the present conditions [19]. Our simulations suggest that the rotational temperature of OCS molecules should be less than 10 K when we observe significant molecular orientation, i.e., significant asymmetry in the TOF spectra.

As mentioned above, since our experiment is performed in an adiabatic regime, we can keep a sample of oriented molecules for a few nanoseconds if we employ a laser pulse with the duration of ~10 ns as used in the present study. Femtosecond or picosecond time-resolved studies including femtosecond timed Coulomb explosion studies [20,21] can be performed on such a sample of oriented molecules. Furthermore, oriented molecules can be used to enhance or suppress some photochemical events whose efficiencies depend on the angle between a specific molecular axis and the polarization direction of the laser field [1].

In conclusion, we have demonstrated clear evidence of the orientation of the OCS molecules. All the results obtained are consistent with one another and compatible with our interpretation that OCS molecules are oriented. Our results show the efficacy of the FH method and the usefulness of our approach to confirm the molecular orientation. It has been recently demonstrated that an intense, elliptically polarized, nonresonant laser field can simultaneously force all three axes of a molecule to align along given axes fixed in space [22]. With an electrostatic field and an elliptically polarized laser field combined, we could expect to realize the three-dimensional orientation of asymmetric top molecules. The alignment and the orientation can be probed by the two-dimensional ion imaging technique and the TOF measurements as presented here, respectively. Such experiments are now in progress in our group. The realization of the three-dimensional orientation should further expand the range of applications in stereodynamical studies of chemical reaction dynamics.

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*Email address: hsakai@phys.s.u-tokyo.ac.jp

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