

Orientation of polar molecules with combined electrostatic and pulsed, nonresonant laser fields

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Received 15 November 2002 / Received in final form 16 January 2003

Published online 24 April 2003 – © EDP Sciences, Società Italiana di Fisica, Springer-Verlag 2003

Abstract. We show that molecules with a moderate permanent dipole moment can be oriented with combined electrostatic and pulsed, nonresonant laser fields. Carbonyl sulfide (OCS) molecules are used as a sample. The degree of orientation can be increased by increasing the peak intensity of the laser field and the magnitude of electrostatic field or by decreasing the initial rotational temperature of the molecules.

PACS. 33.80.-b Photon interactions with molecules – 33.15.Bh General molecular conformation and symmetry; stereochemistry

1 Introduction

The manipulation of atoms and molecules is one of the central subjects in modern physics, chemistry, and biology. The control of the spatial direction of molecules is especially important for studies of steric 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, electric hexapole focusing and strong electrostatic field orientation are used to control the orientation of polar molecules. However, electric hexapole focusing works only for symmetric top molecules and strong electrostatic field orientation is effective only for certain molecules possessing large permanent dipole moments. 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 have been 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 interaction of the permanent dipole moment of the molecules with an electrostatic field and the anisotropic polarizability interaction of the induced dipole moment of molecules with an intense nonresonant laser 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 in-

roduction 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 demonstration 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: (1) 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]. (2) They did not observe any difference when they rotated the laser polarization by 90 degrees. Therefore, it is apparent 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 article, 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.

2 Experimental

The molecular orientation is observed 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

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helium (He) gas through a 0.25-mm-diameter nozzle. The molecular beam is parallel to the TOF axis and crossed at 90 degrees 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 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 estimated to be 2.6×10^{12} W/cm². The 12-ns-long pulses ensure that our experiment is performed in the 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 the window of the TOF spectrometer and a polarizer in the optical path.

We use an intense femtosecond laser pulse (hereafter “probe” pulse) to ionize the OCS molecules at the peak of the YAG pulse to see the instantaneous degree of orientation. The electric signals from the controller for the amplified laser system serve 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 are delivered by 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 estimated to be 3×10^{14} W/cm². The laser pulses are spatially overlapped using a dichroic mirror and focused by a 30-cm-focal-length lens into the 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 $\omega_0^{\text{YAG}} \sim 25$ μm and $\omega_0^{\text{probe}} \sim 14$ μm , respectively. The fragment ions 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 OCS molecules are exposed to an intense femtosecond probe pulse, they Coulomb explode into many small fragments. Each resultant fragment is a rather low flux, ensuring that the MCP operates well below saturation in the present measurements.

3 Results and discussions

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 a natural result of enhanced ionization [13–15] by which molecules

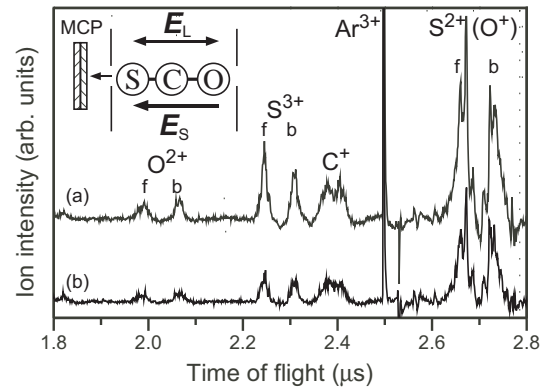


Fig. 1. Typical TOF spectra of OCS molecules (a) with and (b) without Nd:YAG laser pulses. The labels **f** and **b** denote fragment ions coming from the “forward” and the “backward” initial emission directions, respectively. The inset shows the directions of the electrostatic field, the linearly-polarized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

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, ensuring the safe operation of the MCP detector and 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 reveals 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].

When the YAG pulses are applied (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 O atom is 7.3 eV and that of S atom is 6.2 eV. This means that the permanent dipole moment is directed toward S atom and consequently the molecules tend to be oriented in the way shown in the inset of Figure 1. The enhancement of the backward signal is thought to be the result of 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 can be expected, the backward signals are larger than the forward signal when the YAG pulses are applied. When we rotate the polarization of the YAG pulse by 90 degrees, the TOF spectrum remains symmetric. This result shows that the combined effect of parallel fields is crucial for the molecular orientation [8,9].

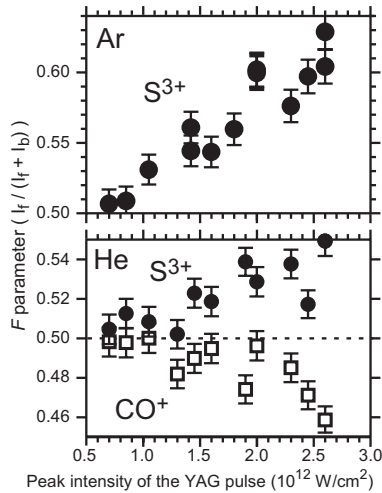


Fig. 2. The dependence of the F parameter (defined in the text) on the peak intensity of the YAG pulse for the fixed electrostatic field of 380 V/cm. The upper panel shows the F parameter of S^{3+} ions from OCS molecules seeded in Ar and the lower panel shows the F parameter of S^{3+} and CO^+ ions from OCS molecules seeded in He. The backing pressure of Ar and He is 8 atm. The error bar given for each point corresponds to the statistical error, *i.e.*, the standard deviation based on the repetitive measurements performed during a relatively short time interval. The double points at the same YAG intensity reflect the reproducibility of the measurements and the time interval between the two measurements is fairly long. The reproducibility is influenced mainly by the degree of spatial overlap of the YAG pulse and the femtosecond probe pulse.

Now we move on to the results of quantitative measurements. There are three key parameters determining the degree of orientation. They are the peak intensity of the YAG pulse, the magnitude of the electrostatic field, and the initial 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 intensity of the YAG pulse is increased and it reaches over 0.60 at 2.6×10^{12} W/cm². 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/cm². The higher degree of orientation

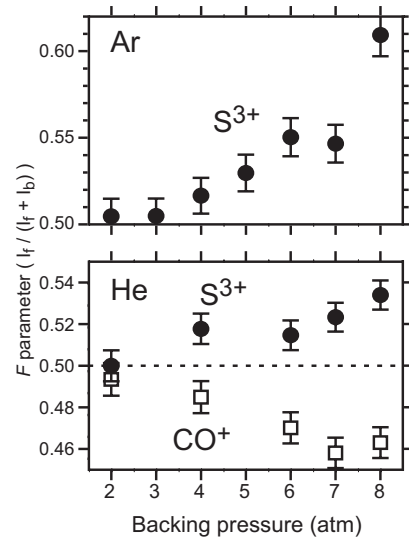


Fig. 3. The dependence of the F parameter (defined in the text) on the backing pressure in the gas valve for the fixed values of the YAG laser intensity (2.6×10^{12} W/cm²) and the electrostatic field (380 V/cm). The upper panel shows the F parameter of S^{3+} ions from OCS molecules seeded in Ar and the lower panel shows the F parameter of S^{3+} and CO^+ ions from OCS molecules seeded in He. The error bar given for each point corresponds to the statistical error, *i.e.*, the standard deviation based on the repetitive measurements performed during a relatively short time interval.

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. We also measure the dependence of the F parameter on the electrostatic field with the fixed YAG laser intensity of 2.6×10^{12} W/cm² and confirm that the changes of the F parameter are consistent with those observed in Figure 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 YAG laser intensity (2.6×10^{12} W/cm²) and the electrostatic field (380 V/cm). The results are summarized in Figure 3. 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. It is necessary to perform a spectroscopic study to accurately determine the rotational temperature of the molecules under the present conditions. We observe no sign of cluster formation. Specifically, we observe no fragment ions originating from clusters. Furthermore, the position (the initial kinetic energy of the fragment ion) and the width of the TOF signal do not change for the backing pressures from 2 to 8 atm. These observations ensure that the cluster formation is virtually negligible.

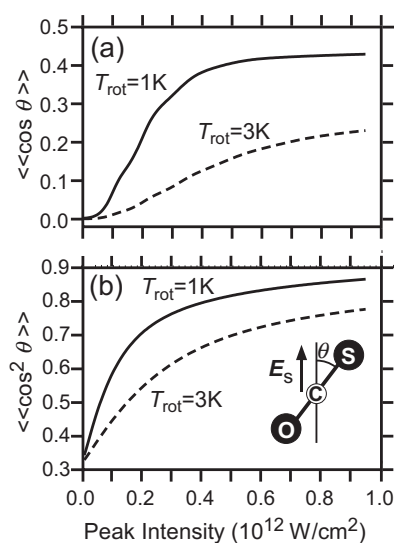


Fig. 4. The ensemble averages of the orientation parameter $\langle\langle \cos \theta \rangle\rangle$ (a) and the alignment parameter $\langle\langle \cos^2 \theta \rangle\rangle$ (b) calculated for OCS molecules as a function of the peak intensity of the laser pulse. The initial rotational temperatures T_{rot} are assumed to be 1 K (solid curves) and 3 K (dashed curves), and the electrostatic field assumed is 380 V/cm. Note that for a sample of randomly oriented molecules the theoretical value of $\langle\langle \cos^2 \theta \rangle\rangle$ is 1/3.

Although the above measurements are performed separately, the results shown in Figures 2 and 3 are consistent with each other, 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 the present experiments are still modest, we can further increase the degree of orientation.

According to the procedure presented by Friedrich and Herschbach [8,9], we have calculated the ensemble averages of the orientation parameter $\langle\langle \cos \theta \rangle\rangle$ and the alignment parameter $\langle\langle \cos^2 \theta \rangle\rangle$, 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). The results are shown in Figure 4. As can be seen in the figure, for the peak laser intensity of 10^{12} W/cm², the electrostatic field of 380 V/cm, 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. These significant values are consistent with the fact that we experimentally observe the molecular orientation. Figure 4a shows that the orientation actually survives Boltzmann averaging though some states including the $J, M = 1, 0$ state are oriented in the “wrong way” [8,9]. Our simulations confirm that it is crucially important to populate the 0,0 state as much as possible by lowering the rotational temperature. A spectroscopic study performed under the similar conditions ensures that the rotational temperature lower than 5 K can be achieved under the present conditions [19]. Our simulations suggest that the rotational temperature of OCS molecules should be less than 10 K when we observe significant molecu-

lar orientation, *i.e.*, significant asymmetry in the TOF spectra.

As mentioned above, since our experiment is performed in the 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. Picosecond or femtosecond 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].

4 Concluding remarks

We have demonstrated clear evidence of the orientation of 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 [22]. It has been demonstrated that an intense, elliptically polarized, non-resonant laser field can simultaneously force all three axes of a molecule to align along given axes fixed in space [23]. 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 [23] and the TOF measurements as presented here, respectively. In this way, we have recently observed the evidence of three-dimensional orientation using 3,4-dibromothiophene molecules as a sample. The details will be presented elsewhere in the near future [24]. The three-dimensional orientation should further expand the range of applications in stereodynamical studies of chemical reaction dynamics.

The authors are grateful to Bretislav Friedrich for his helpful discussions. They also appreciate financial support by Japan Society for the Promotion of Science.

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