

Three Dimensional Alignment of Molecules Using Elliptically Polarized Laser Fields

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We demonstrate, theoretically and experimentally, 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, thus inhibiting the free rotation in all three Euler angles. Theoretically, the effect is illustrated through time dependent quantum mechanical calculations. Experimentally, 3,4-dibromothiophene molecules are aligned with a nanosecond laser pulse. The alignment is probed by 2D ion imaging of the fragments from a 20 fs laser pulse induced Coulomb explosion.

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Control of external degrees of freedom of molecules, their center of mass motion and their orientation in space, is one of the most exciting goals of physical chemistry. In particular, the realization that intense, linearly polarized laser fields of either nonresonant [1] or near-resonance [2] frequencies can induce sharp and controllable alignment has raised substantial experimental [3–5] and theoretical [6–8] interest during the past five years, due to the role of alignment in, e.g., stereodynamical studies and gas-surface research [9].

Nonresonant laser induced alignment results from the interaction between an intense laser field and the induced dipole moment of a molecule. Previous work in this area used linearly polarized fields to inhibit rotation of a molecular symmetry axis with respect to the space-fixed polarization axis. For symmetric top and linear molecules the potential induced by a linearly polarized field depends only on the polar Euler angle, and hence the motion in the two azimuthal angles remains unhindered. For asymmetric tops, motion in the polar angle is sharply aligned and rotation about the body-fixed Z axis is not isotropic. Rotation about the space-fixed z axis remains free. To fully exploit the natural anisotropy of asymmetric top molecules the concept of alignment must therefore be generalized from one to three dimensions.

In this paper we show that an elliptically polarized field can constrain the rotational motion in all three Euler angles of a polyatomic molecule. Three dimensional orientational control is illustrated theoretically and experimentally using 3,4-dibromothiophene (DBT) as an example. A schematic illustration of a one and a three dimensional alignment of DBT is given in Fig. 1.

The Hamiltonian for a rigid molecule subject to a nonresonant field is written as $H = H_{\text{rot}} + H_{\text{ind}}$, where $H_{\text{rot}} = J_a^2/2I_a + J_b^2/2I_b + J_c^2/2I_c$ is the rotational Hamiltonian and I are the principle moments of inertia. $H_{\text{ind}} = -\frac{1}{4} \sum_{\rho, \rho'} \varepsilon_{\rho} \alpha_{\rho\rho'} \varepsilon_{\rho'}$ describes the interaction of the field (ε) with the molecular polarizability tensor (α), and $\rho =$

x, y, z denotes the space-fixed Cartesian coordinates [10]. The space-fixed components of α are related to its body-fixed components, $\alpha_{kk'}$, by $\alpha_{\rho\rho'} = \sum_{kk'} \langle \rho | k \rangle \alpha_{kk'} \langle k' | \rho' \rangle$, where $\langle k | \rho \rangle$ are direction cosines.

For a linear or symmetric top molecule subject to a linearly polarized field ($\alpha_z = \alpha_{\parallel}$, $\alpha_x = \alpha_y = \alpha_{\perp}$; $\varepsilon = \varepsilon_z$) H_{ind} is a function of only one angle, the polar Euler angle θ between the field and the body-fixed Z axis, $H_{\text{ind}} = -\frac{1}{4} \varepsilon^2 (\alpha_{\parallel} - \alpha_{\perp}) \cos^2 \theta$ (apart from an angle independent term which merely shifts all eigenvalues). Similarly, in a

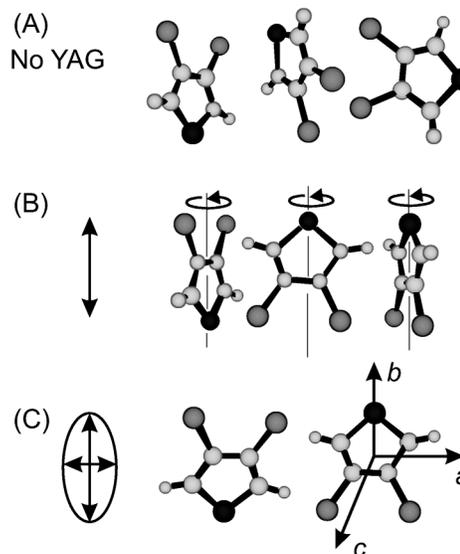


FIG. 1. Illustration of the orientational distribution of 3,4-dibromothiophene (black circles: sulfur, dark grey circles: bromine) molecules for the following: (A) No alignment field present; all orientations are equally likely. (B) A linearly polarized alignment field. The symmetry axis is aligned along the space-fixed axis defined by the alignment field but the molecules are free to rotate around this axis. (C) Elliptically polarized alignment field. All three molecular axes are forced into alignment. The principle inertia axes a, b, c are superimposed on the bottom right model.

circularly polarized field $H_{\text{ind}} = \frac{|e|}{8}(\alpha_{\parallel} - \alpha_{\perp})\cos^2\theta$ (up to a shift), and hence the molecule aligns parallel (perpendicular) to the polarization plane for $\alpha_{\parallel} > \alpha_{\perp}$ ($\alpha_{\parallel} < \alpha_{\perp}$) but its motion in the two azimuthal Euler angles is unhindered. An additional χ dependent term is introduced in the case of an asymmetric top (where χ is the angle of rotation about the body-fixed Z axis) but the motion in χ cannot be independently controlled in either the linear or circular polarization cases. In an elliptically polarized field H_{ind} also depends on ϕ , the angle of rotation about the space-fixed z axis. In particular, for an asymmetric top this provides control over all three Euler angles of rotation.

Quantum mechanically, θ dependence of the field-matter interaction allows for the excitation of a broad superposition of total angular momentum (J) states. χ dependence produces a $\{J, K\}$ superposition, where K is the projection of J onto the body-fixed Z axis. ϕ dependence allows for the excitation of a superposition of M states, M being the projection of J onto the space-fixed z axis.

To quantify the above concepts we solve the time dependent Schrödinger equation by expanding the wave function in a symmetric top basis and propagating a set of coupled differential equations for the expansion coefficients. The pulse duration is chosen sufficiently long (3 ns) to ensure adiabatic evolution. Figure 2 shows the probability density at the peak of the field envelope versus the Euler angles. The body-fixed Z axis is chosen as the b axis (the highest polarizability, C_2 axis [11]) of DBT with the c axis defining the body-fixed X axis. We follow the standard convention of defining the space-fixed z axis parallel to the polarization vector, in the linear case, and perpendicu-

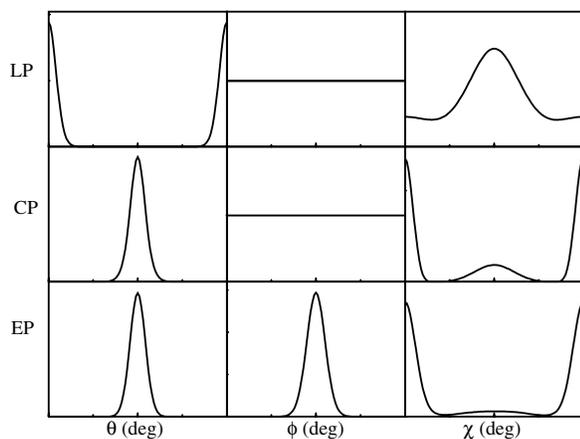


FIG. 2. Probability density at the peak of a 3-ns-long pulse of linear ($I_z = 5.4 \times 10^{11}$ W/cm², top row), circular ($I = 1.1 \times 10^{12}$ W/cm², middle row), and elliptical ($I_x = 2.2 \times 10^{11}$ W/cm², $I_y = 5.4 \times 10^{11}$ W/cm², bottom row) polarization. In each column the dependence on one Euler angle is shown while the other two are integrated over. The initial condition is $J_i = 0$, corresponding to a rotationally cold molecular beam.

lar to the polarization plane, in the cases of circular or elliptical polarization.

The top row of Fig. 2 shows that an intense linearly polarized field sharply aligns the C_2 axis parallel to the polarization axis, $\theta \sim 0, \pi$, leaving the rotation of the molecular plane with respect to the space-fixed $\{x, y\}$ plane (the ϕ dependence) isotropic. Rotation about the C_2 axis (the χ dependence) is only mildly hindered.

The middle row shows that a circularly polarized field leads to strong localizations of the θ and χ distributions, meaning that the molecular plane is confined to the polarization plane. The isotropic ϕ distribution shows, however, that the molecular plane can rotate freely within the polarization plane.

The bottom panel shows that an elliptically polarized field aligns the largest (b) and intermediate (a) polarizability axes along the major (y) and minor (x) polarization axes, corresponding to strongly hindered motion in all three Euler angles. An instructive picture of three dimensional alignment is obtained by describing the elliptically polarized field as the sum of a circularly polarized field and a linearly polarized field, with the former confining the molecule to the polarization plane and the latter restricting the rotation within that plane.

To probe the molecular alignment, we Coulomb explode the DBT molecules with an intense 20 femtosecond (fs) laser pulse synchronized to the peak intensity of the alignment pulse. The short, intense laser pulse multiple ionizes the molecule which subsequently (Coulomb) fragments. The short duration of the laser pulse ensures that the molecular skeleton is left unchanged immediately after the probe pulse [12]. The laboratory frame velocity vector of each fragment is determined by its position in the molecular skeleton and the molecular orientation. In particular, for charge symmetric fragmentation channels the S^+ are ejected along the C_2 axis of the molecule. The direction of S^+ ions hence provides a sensitive probe of the alignment of the C_2 axis [13]. Recently, we introduced this approach in the study of linear alignment by recording the direction of I^+ ions following Coulomb explosion of iodobenzene molecules [5]. The direction of S^+ ions does not reveal any information about the alignment of the molecular plane. This information can be retrieved by recording the Br^+ ions since the structure of DBT implies that these are ejected in the plane of the molecule.

The experimental apparatus used for this setup was described in detail previously [5,14] and only the important features are discussed here. A schematic of the experimental setup is shown in Fig. 3. Briefly, a pulsed supersonic molecular beam is formed by expanding ~ 0.01 bar of DBT seeded in ~ 3 bars of helium into a vacuum chamber through a 0.5 mm nozzle. The molecular beam is intersected by two focused laser beams. One beam originates from a pulsed single longitudinal mode Nd:YAG laser (Coherent Infinity 40-100, $\lambda = 1064$ nm, pulse

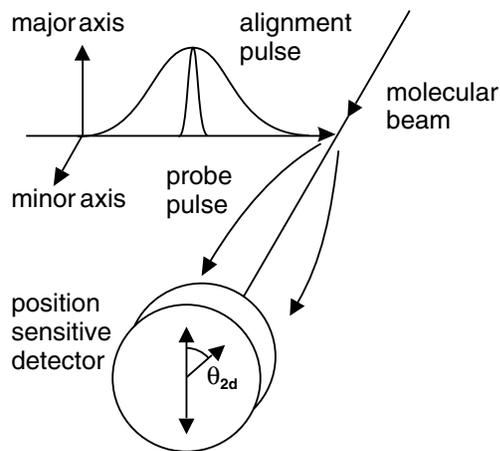


FIG. 3. Schematic overview of the apparatus. The major axis of the YAG polarization is parallel to the detector surface and the minor axis is parallel to the molecular beam.

duration ~ 3.5 ns) and serves as the alignment pulse. A $\lambda/4$ plate is used to gradually change the ellipticity of this pulse from linearly polarized to circularly polarized. The second beam, which probes the alignment by Coulomb explosion of the molecules, consists of circularly polarized 20 fs pulses centered at $\lambda = 800$ nm. The pulses originate from a homebuilt hollow wave guide compressor [15] and their peak intensity is 5×10^{14} W/cm². The direction of the S⁺ and Br⁺ ions are recorded by two dimensional ion imaging [14]. A static field projects the ions onto a position sensitive detector, where charge and mass selected ion images are recorded by a CCD camera.

The experimental results, consisting of the ion images of S⁺ (left column) and Br⁺ (right column) are shown in Fig. 4. The two top images (A) and (A') are recorded without the alignment field. The angular distributions of both S⁺ and Br⁺ fragments are almost circularly symmetric. Quantitatively, the observation is tested by determining the average value of $\langle \cos^2 \theta_{2d} \rangle$ for each ion image [5], θ_{2d} being the angle between the major axis of polarization and the projection of the ion velocity on the detector plane (Fig. 3). For S⁺, $\langle \cos^2 \theta_{2d} \rangle$ yields 0.53 ± 0.04 and for Br⁺ we measure 0.51 ± 0.04 , in agreement with the value of $\frac{1}{2}$ for an isotropic distribution [5,16]. From the isotropic fragmentation pattern of S⁺ and Br⁺ we conclude that the DBT molecules are initially randomly oriented and uniformly probed by the Coulomb explosion technique. Deviations from the circularly symmetric ion images are used to identify alignment.

In the images (B) and (B') the molecules are exposed to a linearly polarized YAG pulse of intensity 5.4×10^{11} W/cm². The pattern of S⁺ ions localizes around the polarization of the YAG pulse (the horizontal axis in the figure) accompanied by an increase of $\langle \cos^2 \theta_{2d} \rangle$ to 0.78 ± 0.04 . We interpret this localization as the result of the DBT molecules being aligned with their C₂ axis parallel to the YAG polarization.

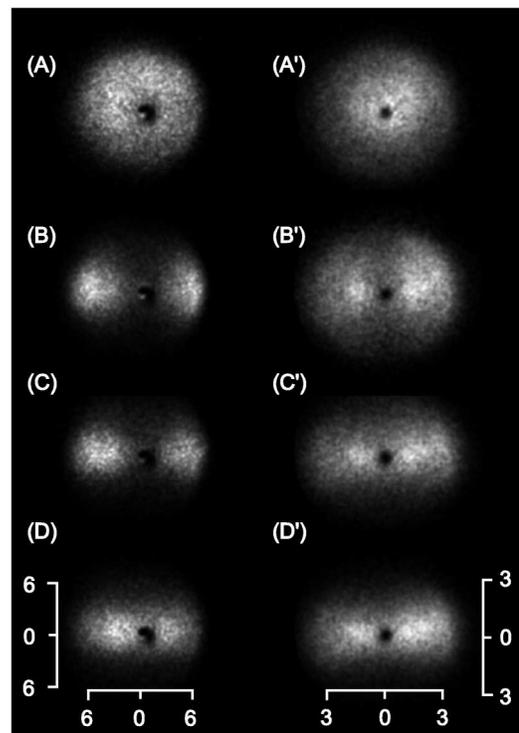


FIG. 4. Ion images of S⁺ (left column) and Br⁺ (right column). The major axis of the YAG polarization is horizontal and the minor axis is perpendicular to the plane of the paper. The central spot in the S⁺ images is O₂⁺ from the background gas. In all images the central portion of the detector is not active. (A),(A') No YAG. (B),(B') Linearly polarized YAG field. (C),(C') Elliptically polarized YAG field. (D),(D') Circularly polarized YAG field. See text for details. The intensities are as in Fig. 2 and the units of the velocity scales are km/s.

Turning to the Br⁺ ion image we observe that the Br⁺ ions are much less localized around the YAG polarization, $\langle \cos^2 \theta_{2d} \rangle = 0.64 \pm 0.04$. This is consistent with the predictions of our calculations that in the presence of the linearly polarized alignment field the ϕ distribution is isotropic (Fig. 2). The Coulomb fragmentation of the linearly aligned molecules leads to the ejection of Br⁺ ions in a cone with the YAG polarization as the center line.

Figures 4(C) and 4(C') show ion images when DBT is exposed to an elliptically polarized YAG field. The intensity along the major axis of polarization (horizontal in the image) is kept equal to the intensity of the linearly polarized pulse in Figs. 4(B) and 4(B') at 5.4×10^{11} W/cm². An additional field with intensity 2.2×10^{11} W/cm² is added along the minor axis (perpendicular to the plane of the paper). The pattern of S⁺ ions is almost identical to the previous image recorded with a linearly polarized YAG pulse, Fig. 4(B). In particular $\langle \cos^2 \theta_{2d} \rangle$ is still 0.78 ± 0.04 . This confirms the theoretical prediction that, in an elliptically polarized alignment field, DBT aligns with its C₂ axis along the major component of the field. Next, by comparing the Br⁺ images of (B') and (C') we observe that the elliptically polarized YAG pulse squeezes

all of the Br^+ ions to a narrow band parallel to the major axis of YAG polarization. We interpret this localization of Br^+ as the DBT molecules being aligned with the molecular plane in the polarization plane of the YAG pulse.

Together, Figs. 4(C) and 4(C') illustrate that the molecular plane is aligned with the polarization plane of the YAG pulse. The axis of largest polarizability, the C_2 axis of the molecule, is aligned along the major axis of the YAG polarization, as predicted by our calculations.

Finally, Figs. 4(D) and 4(D') are ion images recorded with a circularly polarized YAG pulse. The YAG intensity is $1.1 \times 10^{12} \text{ W/cm}^2$, again ensuring that the electrical field component along the major axis is kept constant. The Br^+ image, Fig. 4(D'), is almost identical to Fig. 4(C'). In particular, the Br^+ ions are still squeezed into a narrow band showing that the molecular plane is still confined to the polarization plane [17]. However, the S^+ image has changed from the two localized regions in Fig. 4(C) to a narrow band similar to the Br^+ image. This shows that the S^+ ions are ejected in the polarization plane rather than along the major axis. We conclude that the molecular plane is aligned with the polarization plane but the molecule can rotate freely around an axis perpendicular to the molecular plane, in agreement with our calculations (Fig. 2).

It is crucial for the interpretation of alignment that the degree of localization of the direction of the fragments decreases as the rotational temperature of the molecules is increased or if the intensity of the alignment laser is lowered [1–5]. We confirmed that the alignment recorded for the laser conditions of Fig. 4, deteriorated both by increasing the rotational temperature (by lowering the helium pressure in the supersonic expansion [18]) and by lowering the intensity of the YAG pulse.

In conclusion, we have demonstrated, theoretically and experimentally, that three dimensional alignment of molecules using elliptically polarized laser fields is feasible. Qualitative agreement between theory and experiment was found. In the near future we expect to quantify the comparison by modifying our detection scheme and generalizing the calculations to account for temperature. Experimental and theoretical results indicating three dimensional alignment were also obtained for *o*-dibromobenzene and tetrachloroethylene. We stress that, although a planar molecule was chosen for this work, the technique is applicable to any molecule possessing an anisotropic polarizability. In particular, the ellipticity of the alignment field can be tailored to the polarizability tensor of an arbitrary molecule to give a desired three dimensional alignment.

Among the variety of exciting new opportunities introduced by the ability of intense lasers to inhibit the rota-

tional motions of molecules, we mention stereodynamical studies free of rotational averaging [9] and improved selectivity in photoexcitations [19] which could facilitate the measurement of transition dipole moments of biological species [20].

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