Three dimensional orientation of small polyatomic molecules excited by two-color femtosecond pulses

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Abstract

We study the excitation of asymmetric-top (including chiral) molecules by two-color femtosecond laser pulses. In the cases of non-chiral asymmetric-top molecules excited by an orthogonally polarized two-color pulse, we demonstrate, classically and quantum mechanically, three-dimensional orientation. For chiral molecules, we show that the orientation induced by a cross-polarized two-color pulse is enantioselective along the laser propagation direction, namely, the two enantiomers are oriented in opposite directions. The classical and quantum simulations are in excellent agreement on the short time scale, whereas on the longer time scale, the enantioselective orientation exhibits quantum beats. These observations are qualitatively explained by analyzing the interaction potential between the two-color pulse and molecular (hyper-)polarizability. The prospects for using the enantioselective orientation for enantiomers’ separation is discussed.

Keywords: two-color femtosecond pulse, three-dimensional orientation, enantioselective orientation, asymmetric-top molecule, chiral molecule

(Some figures may appear in colour only in the online journal)

1. Introduction

Molecular alignment and orientation have attracted widespread interest due to their importance in chemical reaction control, ultra-fast imaging of molecular structure and dynamics, and photon-induced molecular processes.

Notable examples, to name a few, are the utilization of ultra-short laser pulses to induce field-free three-dimensional (3D) alignment of gas-phase molecules [1–6], and of small molecules trapped in helium droplets, e.g. see [7]; or the use of terahertz (THz) pulses to prepare oriented samples of polar symmetric [8, 9] and asymmetric-top [10, 11] molecules under field-free conditions. For extensive reviews of the molecular alignment and orientation, see [12–17]. The dynamics of molecular alignment has also been studied using state-resolved spectroscopic techniques, e.g. molecular fluorescence [18], air lasing [19] and absorption spectroscopy [20]. An additional efficient tool for inducing molecular orientation is non-resonant phase-locked two-color laser pulses consisting of the fundamental wave...
(FW) and its second harmonic (SH). Two-color pulses have been shown, both theoretically and experimentally, to be effective for orienting linear molecules [21–35]. Recently, we theoretically considered the orientation of symmetric-top molecules excited by femtosecond two-color pulses [36], and previously experimentally demonstrated field-free 3D orientation induced by orthogonally polarized femtosecond two-color pulses [37].

A unique class of asymmetric-top molecules is formed by the chiral molecules. A chiral molecule has two forms, called left- and right-handed enantiomers. Control schemes enabling manipulating specific enantiomers are called enantioselective. Following a series of theoretical works [38–41], the enantioselective orientation of chiral molecules was demonstrated experimentally [42, 43] using the optical centrifuge for molecules [44–48]. Most recently, THz pulses with twisted polarization were theoretically shown to induce enantioselective orientation as well [49].

This paper considers the orientation of asymmetric-top (including chiral) molecules excited by two-color femtosecond laser pulses. We begin by analyzing molecules belonging to the $C_{2v}$ point group, including formaldehyde and sulfur dioxide as typical examples, excited by orthogonally polarized two-color pulses. In these cases, the two-color pulse excitation gives rise to both 3D alignment and orientation of the permanent molecular dipole moment. We also consider the chiral molecule (lacking any symmetry except $C_1$) excited by orthogonally polarized two-color pulses. Then, we investigate the orientation of chiral molecules excited by pulses with general cross-polarization, where the FW and SH polarizations are neither parallel nor orthogonal. In this case, the induced orientation is shown to be enantioselective. The paper is organized as follows: in the next section, we summarize our numerical methods. In section 3, we present the three-dimensional molecular alignment/orientation and the long-lasting orientation induced by the orthogonally polarized two-color pulse. In section 4, we discuss the enantioselective orientation of chiral molecules, and finally, section 5 concludes the paper.

2. Numerical methods

We consider the asymmetric-top molecules as rigid rotors. The electric field of two-color laser pulses, consisting of the FW and its SH, is modeled by

$$E(t) = \varepsilon_1(t) \cos(\omega t) e_x + \varepsilon_2(t) \cos(2\omega t) e_{SH},$$

where $\varepsilon_n(t) = \varepsilon_n,0 \exp[-2\ln 2(t/\sigma_n)^2]$, $n = 1, 2$, is the field’s envelope, $\varepsilon_n,0$ is the peak amplitude, and $\sigma_n$ is the full width at half maximum. Here, $\omega$ is the carrier frequency of the FW field, $e_{SH} = \cos(\phi_{SH}) e_x + \sin(\phi_{SH}) e_y$, where $\phi_{SH}$ is the angle between the polarizations of the FW and SH fields, and $e_x$ and $e_y$ are unit vectors along the laboratory X and Y axes, respectively. The FW and SH are assumed to be phase-locked, and the relative phase between them is set to zero.

Simulations of the laser-driven molecular rotations were carried out both classically and fully quantum mechanically. An extended description of our numerical approaches can be found in [36].

2.1. Classical simulation

The rotation of a classical rigid body is described by Euler’s equations [50]

$$\dot{\mathbf{\Omega}} = (\mathbf{I} \mathbf{\Omega}) \times \mathbf{\Omega} + \mathbf{T},$$

where $\mathbf{I} = \text{diag}(I_a, I_b, I_c)$ is the moment of inertia tensor (here, $I_a < I_b < I_c$), $\mathbf{\Omega} = (\Omega_x, \Omega_y, \Omega_z)$ is the angular velocity, and $\mathbf{T} = (T_x, T_y, T_z)$ is the external torque, $x \times y$ denotes vector cross-product. All quantities in equation (2) are expressed in the molecular reference frame where the basis comprises the three principal axes of inertia, $a, b, c$. When external electric fields couple to a rigid body via its polarizability and hyperpolarizability, the torque is given by

$$\mathbf{T} = \alpha \mathbf{E} \times \mathbf{E} + \frac{1}{2} (\beta \mathbf{E} \times \mathbf{E}) \times \mathbf{E},$$

where $\alpha$ and $\beta$ are the polarizability and hyperpolarizability tensors, respectively, and $\mathbf{E}$ is the electric field vector. The time-dependent relation between the laboratory and molecular reference frames is parametrized by a quaternion, $q$ [51, 52]. Quaternions obey the equation of motion $\dot{q} = q\Omega/2$, where $\Omega$ is a quaternion composed of the molecule’s angular velocity components [51, 52]. To simulate the behavior of a thermal ensemble consisting of $N \gg 1$ non-interacting molecules, we use the Monte Carlo method. For each molecule, we numerically solve a system of coupled equations consisting of Euler’s equations (equation (2)), including the torque in equation (3), and the equation of motion of the quaternion. The initial state, in which the molecules are isotropically distributed in space, is modeled using random uniform quaternions generated according to the recipe in [53]. Initial molecular angular velocities are given by the Boltzmann distribution,

$$f(\mathbf{\Omega}) \propto \prod_i \exp \left( -\frac{I_i \Omega_i^2}{2k_B T} \right),$$

where $i = a, b, c$, $k_B$ is the Boltzmann constant, and $T$ is the temperature.

2.2. Quantum simulation

The Hamiltonian describing the rotational dynamics of a molecule driven by two-color fields is $H(t) = H_r + H_{int}(t)$, where $H_r$ is the field-free Hamiltonian [54] and the molecule–field interaction potential, including the polarizability and hyperpolarizability contributions, is given by [55]

$$H_{int}(t) = -\frac{1}{2} \sum_{ij} \alpha_{ij} E_i E_j - \frac{1}{6} \sum_{ijk} \beta_{ijk} E_i E_j E_k.$$ 

Here $E_i$, $\alpha_{ij}$, and $\beta_{ijk}$ represent the components of the field vector, polarizability tensor, and hyperpolarizability tensor, respectively.

For the calculations, we use the basis set of field-free symmetric-top wave functions $|JKM \rangle$ [54]. Here $J$ is the total angular momentum, $K$ and $M$ are the projections onto the
molecule-fixed $a$ axis and the laboratory-fixed $Z$ axis, respectively. The non-zero matrix elements of the field-free Hamiltonian of asymmetric-top molecules are given by [54]

$$
\langle JKM|H_r|JKM \rangle = \frac{B + C}{2} [J(J + 1) - K^2] + AK^2,
$$
$$
\langle JKM|H_r|JK \pm 2M \rangle = \frac{B - C}{4} f(J, K, \pm 1),
$$

(6)

where $f(J, K) = \sqrt{(J^2 - K^2)(J + 1)^2 - K^2}$ and the rotational constants are $A = h^2/2I_\tau$, $B = h^2/2I_b$, and $C = h^2/2I_c$ with $A > B > C$.

The eigenfunctions of the asymmetric top are obtained numerically by diagonalizing the field-free Hamiltonian $H_r$. The eigenfunctions can be written as $|J\tau M\rangle = \sum_k c_k^{(J\tau M)}|JKM\rangle$ (see equation (6)), where $-J \leq \tau \leq J$ enumerates the asymmetric-top eigenstates for a given $J, M$ quantum numbers. We set the initial state as $|\Psi(t = 0)\rangle = |J\tau M\rangle$ and solve the time-dependent Schrödinger equation $i\hbar \partial_t|\Psi(t)\rangle = H(t)|\Psi(t)\rangle$ using numerical exponentiation of the Hamiltonian matrix (see Exopkit [56]).

The expectation value of the dipole signal along a direction defined by $\vec{e}$, a unit vector in the laboratory-fixed frame, is given by

$$
\langle \mu_i^{(J\tau M)}(t) \rangle = \langle \Psi(t)|\vec{\mu} \cdot \vec{e}|\Psi(t)\rangle,
$$

(7)

where $\vec{\mu}$ is the molecular dipole moment vector.

Thermal effects are included by averaging the expectation value over the different initial states $|J\tau M\rangle$ with the relative weight given by the Boltzmann distribution,

$$
\langle \mu_i \rangle = \frac{1}{Z} \sum_{J\tau M} \exp \left(-\frac{\varepsilon_{J\tau M}}{k_B T}\right) \langle \mu_i^{(J\tau M)} \rangle(t),
$$

(8)

where $Z = \sum_{J\tau M} \exp \left(-\frac{\varepsilon_{J\tau M}}{k_B T}\right)$, and $\varepsilon_{J\tau M}$ is the energy of $|J\tau M\rangle$.

3. Three-dimensional alignment and orientation

In this section, we consider two relatively simple (non-chiral) asymmetric-top molecules, formaldehyde (CH2O) and sulfur dioxide (SO2), and a chiral molecule—propylene oxide (PPO, CH3CHCH2O), excited by an orthogonally polarized two-color pulse. The polarizations of the FW and SH fields are set along the $X$ and $Y$ axes, respectively. Molecular orientations of CH2O, SO2, and PPO are summarized in table 1. Moments of inertia from NIST (DFT, method: CAM-B3LYP/aug-cc-pVTZ) [57], while the other parameters of CH2O were taken from [58] (DFT, method: B3LYP/aug-cc-pVTZ). The parameters of SO2 are taken from the literature [59]. Molecular properties of (R)-PPO (right-handed enantiomer) were calculated using GAUSSIAN [60] (method: CAM-B3LYP/aug-cc-pVTZ). The two enantiomers, (R)-PPO (right-handed) and (S)-PPO (left-handed), are mirror images of each other [61] and here we choose the $ab$-plane as the plane of reflection. The results are independent of the choice of the reflection plane. Figure 1 presents graphical images of the molecules with their principal axes of inertia.

Since CH2O and SO2 are planar molecules belonging to the $C_2v$ point symmetry group (see figure 1), according to spin-statistics theorem, additional spin statistical factor should be included in the sum in equation (8). In the case of CH2O molecule, initial rotational $|J\tau M\rangle$ states formed by $|J\tau M\rangle$ states with an odd quantum number $K$ (antisymmetric with respect to $\pi$-rotation about the $a$ axis) have triple the statistical weight compared with $|J\tau M\rangle$ states formed by symmetric-top states with even $K$ (symmetric with respect to $\pi$-rotation about the $a$ axis). For details, see the introduction of [62]. For SO2 molecule, only states symmetric with respect to $\pi$-rotation about the $b$ axis (dipole moment) are taken into account [63].

3.1. Formaldehyde

Figure 2(a) shows the classically calculated degrees of alignment of CH2O molecules during and shortly after the excitation by a femtosecond two-color pulse. The degrees of alignment are quantified by averages of squares of directional cosines, $\cos^2(\theta_{ij})$, where $\theta_{ij}$ represents the angle between the molecular $i$ axis and the laboratory $j$ axis. Here, the initial temperature is $T = 5$ K, the peak intensities of the FW and SH fields are $I_{FW} = 2 \times 10^{13}$ W cm$^{-2}$ and $I_{SH} = 8 \times 10^{13}$ W cm$^{-2}$, the duration is $\sigma_{FW} = \sigma_{SH} = 100$ fs, and $\phi_{SH} = \pi/2$ (see equation (1)). As can be seen, shortly after the pulse (at $t \approx 0.2$ ps), all three molecular axes are simultaneously aligned along the three laboratory axes. The molecular $a$ axis is aligned along the laboratory $Y$ axis, while the $b$ and $c$ axes are aligned along the $X$ and $Z$ axes, respectively. Similar 3D alignment was achieved using a single one-color elliptically polarized laser pulse [1, 4, 6, 7], or a pair of delayed cross-polarized one-color pulses [2, 3]. In the case of two-color pulses used here, the strong SH field aligns the most polarizable $a$ axis along the laboratory $Y$ axis (see the oxygen atom (red) in the inset of figure 2(a)), while the weak FW field aligns the second most polarizable $b$ axis (the intermediate axis of inertia) along the $X$ axis (see hydrogen atoms (gray) in the inset of figure 2(a)). Finally, due to the geometric constraints, the $c$ axis is aligned along the $Z$ axis, resulting in the 3D alignment.

Moreover, figure 2(b) shows the calculated (both classically and quantum mechanically) expectation value of the projection of the dipole moment on the laboratory $Y$ axis, $\langle \mu_Y \rangle(t)$. The degrees of orientation of all the molecular axes along the
Table 1. Molecular properties (in atomic units) of CH$_2$O, SO$_2$, and PPO: moments of inertia, non-zero elements of dipole moment, polarizability tensor, and hyperpolarizability tensor in the frame of molecular principal axes of inertia.

| Molecules      | Moments of inertia | Dipole components | Polarizability components | Hyperpolarizability components |
|----------------|--------------------|-------------------|--------------------------|--------------------------------|
| Formaldehyde CH$_2$O | $I_a = 11560$ | $\mu_a = -0.948$ | $\alpha_{aa} = 22.64$ | $\beta_{aaa} = 47.0$ |
|                | $I_b = 84122$   |                   | $\alpha_{bb} = 14.16$ | $\beta_{abb} = 62.9$ |
|                | $I_c = 95682$   |                   | $\alpha_{cc} = 16.03$ | $\beta_{acc} = 10.3$ |
|                | $I_a = 55509$   |                   | $\alpha_{aa} = 31.26$ | $\beta_{aaa} = 22.0$ |
| Sulfur dioxide SO$_2$ | $I_b = 317477$ | $\mu_b = -0.7877$ | $\alpha_{bb} = 20.80$ | $\beta_{bbb} = 62.5$ |
|                | $I_c = 371885$  |                   | $\alpha_{cc} = 18.64$ | $\beta_{ccc} = 6.4$ |
| (R)-PPO        | $I_a = 180386$  | $\mu_a = 0.380$  | $\alpha_{aa} = 45.63$ | $\beta_{aaa} = 32.18$ |
|                | $I_b = 371885$  | $\mu_b = -0.682$ | $\alpha_{bb} = 37.96$ | $\beta_{abb} = -0.057$ |
|                | $I_c = 553513$  | $\mu_c = 0.192$  | $\alpha_{cc} = 37.87$ | $\beta_{ccc} = 7.05$ |
| (S)-PPO        | $I_a = 180386$  | $\mu_a = 0.380$  | $\alpha_{aa} = 2.56$  | $\beta_{aaa} = 8.61$ |
|                | $I_b = 493185$  | $\mu_b = -0.682$ | $\alpha_{bb} = -0.85$ | $\beta_{abb} = -10.79$ |
|                | $I_c = 84122$   | $\mu_c = -0.192$ | $\alpha_{cc} = -0.65$ | $\beta_{ccc} = 2.38$ |

Figure 2. (a) Classically calculated degrees of alignment for CH$_2$O molecule. The overall degree of alignment is defined as 
$\langle \cos^2 \theta_{\phi} \rangle = \langle 1 + \langle \cos^2 \theta_{\phi} \rangle + \langle \cos^2 \theta_{\theta} \rangle + \langle \cos^2 \theta_{\chi} \rangle \rangle / 4$ (dashed black). The inset illustrates the 3D alignment and orientation along the SH direction (notice, more oxygen atoms point down). (b) $Y$ projection of the dipole signal. Solid blue and dotted red lines are the results of quantum and classical simulations, respectively. Solid green line is the moving time average defined by $\langle \langle \mu \rangle \rangle\langle t \rangle = \langle \Delta t \rangle^{-1} \int \Delta t d't \langle \mu \rangle\langle t' \rangle$, where $\Delta t = 100$ ps. The inset shows a magnified portion of the signals. Here, initial temperature is $T = 5$ K, the angle between the polarizations of FW and SH is $\phi_{\text{SH}} = \pi / 2$. $N = 10^5$ molecules are used in the classical simulation.

X and Z axes are identically zero. Both the quantum and classical results show the transient dipole orientation along the $-Y$ direction following the kick by the two-color femtosecond pulse.

Both the 3D alignment and orientation of the dipole moment can be understood by analyzing the field-polarizability interaction potential (see equation (5)), which can be expressed in terms of the three Euler angles $\phi, \theta, \chi$. Here, we adopt the convention used in [54], according to which $\phi$ and $\theta$ are the azimuthal and polar angles of the molecule-fixed $z$ axis ($a$ axis used here) with respect to the laboratory-fixed $X$ and $Z$ axes, respectively, and $\chi$ represents the additional rotation angle around the $z$ axis (see figure 3(a)). For the orthogonally polarized two-color pulse used here,

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after averaging over the optical cycle, the field-polarizability interaction potential breaks into two independent parts (see equation (A.1)): (i) the interaction with the FW field, and (ii) the interaction with the SH field.

In the case of CH$_2$O molecule, the field-polarizability interaction potential (see equation (A.1)) has four global minima at $M_1 = (\phi_1, \theta_1, \chi_1)$, where $M_1 = (\pi/2, \pi/2, \pi/2)$, $M_2 = (\pi/2, \pi/2, 3\pi/2)$, $M_3 = (3\pi/2, \pi/2, \pi/2)$, and $M_4 = (3\pi/2, \pi/2, 3\pi/2)$. Taking $M_1$ as an example, figure 3(a) shows the sequence of rotations bringing the molecule-fixed frame into the orientation defined by $M_1$. All four orientations of the molecule-fixed frame are shown in figure 3(b), which together produce 3D alignment as illustrated in the inset of figure 2(a).

In terms of the transformation relating the laboratory-fixed and molecule-fixed frames of reference, $U(\phi, \theta, \chi)(b, c, a)^T = (X, Y, Z)^T$ (see equation (B.1)), for the molecular dipole moment, the four minima satisfy

\[
U(M_1)\mu^T = U(M_2)\mu^T = (0, -0.948, 0)^T, \\
U(M_3)\mu^T = U(M_4)\mu^T = (0, +0.948, 0)^T,
\]

which means that the molecular dipole moment ($\mu \propto -a$) is aligned along the laboratory $Y$ axis, see figure 3(b). Similarly, it can be shown that the $b$ and $c$ axes are aligned along the $X$ and $Z$ axes, respectively.

Unlike the symmetric field-polarizability interaction, which has two independent contributions from the FW and SH, the field-hyperpolarizability interaction potential couples the FW and SH fields. This results in an asymmetric interaction potential causing orientation of the dipole moment. The field-hyperpolarizability interaction potential (see equation (A.2)) has two global minima at $M_1$ and $M_2$. Since

\[
U(M_1)\mu^T = U(M_2)\mu^T = (0, -0.948, 0)^T,
\]

the symmetry along the laboratory $Y$ axis is broken, resulting in an imbalance of the dipole moments along the $Y$ direction versus those pointing along the $-Y$ direction (see figure 3(b)). Notice that the orientation is along the polarization direction of the SH field. For molecules belonging to the $C_{2v}$ point symmetry group, the combination of 3D alignment and orientation of one of the molecular axes results in the 3D orientation.

The inset in figure 2(a) summarizes the foregoing discussion. Note that initially there is a small orientation along the $-Y$ direction, in accordance with the potential analysis. However, due to its relatively small moments of inertia (see table 1), the CH$_2$O molecule rotates relatively fast, resulting in a rapid change of orientation direction from $-Y$ to $Y$. Following the pulse, when the field-free 3D alignment appears at $t \simeq 0.2$ ps, the orientation of the dipole moment is along the $Y$ direction.

On the long time scale, in addition to the transient effect of 3D orientation, there is a residual orientation lasting long after the end of the pulse, see the inset in figure 2(b). In contrast to the classically calculated orientation signal, the quantum one exhibits quantum beats [64–67]. For asymmetric-top molecules, there are several types of revivals [68, 69]; and the restoration of the rotational wave packet during the revivals is not perfect, resulting in the complex quantum beats picture. Despite the beats, the moving time average of this signal, like in the classical case, remains non-zero. Related effects of long-lasting orientation were analyzed and implemented using other orientation schemes [9, 36, 41–43, 49]. The existence of a non-zero time-averaged dipole signal relies on the combination of two factors: (i) the ability of symmetric/asymmetric-top molecules to precess about the conserved angular momentum vector and (ii) the symmetry breaking which is induced by the electromagnetic interaction. Here, the molecular $a$ axis ($\mu \propto -a$) performs a precession-like motion about the polarization direction of the SH field, contributing to the long-lasting dipole orientation.

The eigenstates of asymmetric-top molecules, $|J\tau M\rangle$ do not have a well-defined projection of the angular momentum on the molecular $a$ axis (unlike the eigenstates of symmetric-top molecules, $|JK\rangle$). This leads to the decay of the long-lasting orientation and eventual change of its sign. However, as we show here, the time scale of this process exceeds the duration of the excitation pulse by orders of magnitude.

Whenever the two-color field–molecule interactions involve ionization, preferential ionization of the molecules leads to laser-induced orientation. This ionization-induced orientation of linear molecules was studied in detail in [28–30], and was also observed in [37] for asymmetric-top molecules. Based on these studies, the orientation induced by hyperpolarizability and ionization mechanisms, in principle, can be distinguished on the short time scale. In accordance with [37] and for the conditions of the current work, the ionization-induced orientation of SO$_2$ molecules at intensities $\lesssim 10^{14}$ W cm$^{-2}$ is much smaller than the hyperpolarizability-induced orientation discussed here (see section 3.2). More generally, the relative importance of the two mechanisms depends on the details of the molecular structure and laser field parameters, e.g. relative polarization of the FW and SH. A full, detailed investigation of the dependence on laser intensities and molecular structure is beyond the scope of the current work.

### 3.2. Sulfur dioxide

Figure 4(a) shows that shortly after the end of the two-color pulse excitation, at $t \simeq 0.3$ ps, the SO$_2$ molecules are 3D aligned as illustrated in the inset. Here $I_{FW} = 8 \times 10^{13}$ W cm$^{-2}$ and $I_{SH} = 2 \times 10^{13}$ W cm$^{-2}$, so that the strong FW aligns the most polarizable $a$ axis (see oxygen atoms (red) in the inset of figure 4(a)), while the weak SH field aligns the second most polarizable $b$ axis [see the sulfur atom (yellow)]. In addition, as shown in figure 4(b), the dipole signal is along the $-Y$ direction at $t = 0.3$ ps. This means that there are more molecular dipoles [see the sulfur atom (yellow)] pointing along the $-Y$ direction.

For the case considered here, when the FW is stronger than the SH, the field-polarizability potential (see equation (A.1)) has four global minima at $M_1 = (0, \pi/2, \pi/2)$, $M_2 = (0, \pi/2, 3\pi/2)$, $M_3 = (\pi, \pi/2, \pi/2)$, and $M_4 = (\pi, \pi/2, 3\pi/2)$. Like in the case of CH$_2$O molecule, the existence
Figure 3. (a) A sequence of three Euler rotations (according to convention of [54]) bringing the molecule-fixed frame (bca) into the orientation corresponding to one of the four global minima, $M_1 = (\pi/2, \pi/2, \pi/2)$. (b) Orientations of the molecule-fixed frame defined by four global minima, $M_i$. The dipole moment is $\mu \propto -a$.

Figure 4. (a) Classically calculated degrees of alignment and (b) $Y$ projection of the dipole signal for SO$_2$ molecule. The conditions used are the same as in figure 2, except that $I_{FW} = 8 \times 10^{13}$ W cm$^{-2}$ and $I_{SH} = 2 \times 10^{13}$ W cm$^{-2}$. The overall degree is defined as $\langle \cos^2 \delta \rangle = (1 + \langle \cos^2 \theta_{ax} \rangle + \langle \cos^2 \theta_{by} \rangle + \langle \cos^2 \theta_{cz} \rangle) / 4$ (dashed black).

of these minima implies 3D alignment. Moreover, the total potential, including the field-hyperpolarizability interaction (see equation (A.3)) has only two global minima at $M_1$ and $M_4$. Since

$$U(M_1)\mu^T = U(M_4)\mu^T = (0, -0.7877, 0)^T,$$

the two-color pulse kicks the dipole moment ($\mu \propto -b$) toward the $-Y$ direction. This results in 3D orientation as shown in the inset of figure 4(a).

Furthermore, both the classical result and moving time average of the quantum signal show no long-lasting dipole orientation, see the inset in figure 4(b). As was mentioned previously (see also [9]), one of the requirements for the long-lasting/persistent orientation is the ability of symmetric- and asymmetric-top molecules to precess about the conserved vector of angular momentum. Here, by precession or precession-like motion, we mean that the tip of one of the molecular axes moves on a closed trajectory around the conserved vector of angular momentum. Consequently, the precessing vectors have a constant sign projection along the direction of angular momentum in asymmetric-top molecules, such trajectories exist only for the two molecular axes with the lowest and highest moments of inertia, the $a$ and $c$ axes, respectively [50, 70]. The projection of the intermediate axis, $b$ along the direction of angular momentum does not conserve its sign, resulting in
Figure 5. (a) Classically calculated degrees of alignment and (b) Y projection of the dipole signal for PPO molecule. The conditions used are the same as in figure 4. The overall degree is defined as \( \langle \cos^2 \delta \rangle = \frac{1}{4} \left( \langle \cos^2 \theta_{\alpha X} \rangle + \langle \cos^2 \theta_{\beta Z} \rangle + \langle \cos^2 \theta_{\gamma Y} \rangle \right) \) (dashed black). Note that the results of both enantiomers, (R)- and (S)-PPO are the same.

3.3. Propylene oxide

Figure 5(a) shows that shortly after the end of the two-color pulse excitation, at \( t \approx 0.5 \) ps, the PPO molecules are 3D aligned as illustrated in the inset. Here, the strong FW aligns the most polarizable \( \alpha_1 \) axis, while the weak SH field aligns the second most polarizable \( \alpha_2 \) axis. For (R)-PPO molecule, in the basis of inertia principal axes \( b, c, a \), \( \alpha_1 = (0.293, 0.115, 0.949) \), \( \alpha_2 = (0.394, 0.890, -0.229) \), and \( \alpha_3 = (-0.872, 0.441, 0.215) \). Therefore, the molecular \( a \) axis (which is close to the \( \alpha_1 \) axis) is aligned along the \( X \) axis, while the molecular \( c \) axis (which is close to the \( \alpha_2 \) axis) is aligned along the \( Y \) axis. Due to the geometric constraints, the \( b \) axis is aligned along the \( Z \) axis, resulting in the 3D alignment.

In addition, figure 5(b) shows the dipole signal along the \( Y \) direction, \( \langle \mu_Y \rangle \). Note that \( \langle \mu_X \rangle \) and \( \langle \mu_Z \rangle \) are identically zero. For (R)-PPO, the field-hyperpolarizability interaction potential induced by the orthogonally polarized two-color pulse (same as in figure 4) has two global minima at \( M_1^{(R)} \approx (0.24\pi, 0.25\pi, 1.28\pi) \) and \( M_2^{(R)} \approx (0.76\pi, 0.75\pi, 0.28\pi) \). Accordingly,

\[
U \left[ M_1^{(R)} \right] [\mu]^{(R)} T \approx (0.22, 0.76, -0.14)^T,
\]

\[
U \left[ M_2^{(R)} \right] [\mu]^{(R)} T \approx (-0.22, 0.76, 0.14)^T,
\]

where \( \mu^{(R)} \) is the dipole moment vector of the \( (R) \)-PPO molecule. This shows that the two-color pulse kicks the molecular dipole moment toward two directions, \( (0.22, 0.76, -0.14) \) and \( (-0.22, 0.76, 0.14) \) in the laboratory frame, such that the net dipole signal is along the \( Y \) direction. The same is true for the case of (S)-PPO molecule. Although smaller compared to the case of formaldehyde, the long-lasting orientation also appears, as is shown in the inset in figure 5(b).

In the case of chiral molecules (lacking any symmetry except \( C_1 \)), 3D orientation requires not only 3D alignment and orientation of the dipole moment, but the orientation of all three molecular axes. Previously, 3D orientation of chiral molecules was studied using time-independent cross-polarized two-color laser fields in which the polarizations of the FW and SH fields are neither parallel nor orthogonal [74].

4. Enantioselective orientation effect

In this section, we consider the orientation of chiral molecules excited by a cross-polarized two-color laser pulse. We use the propylene oxide molecule (PPO, CH\(_3\)CHCH\(_2\)O), as a typical example. When the relative angle between the polarization is
not an integer multiple of $\pi/2$, the induced orientation of chiral molecules is enantioselective. As an example, we consider the case of $\phi_{SH} = \pi/4$ (see equation (1)), namely the polarization of the FW is along the $X$ axis and the polarization of the SH is directed at an angle of $\pi/4$ with respect to the $X$ axis. For the molecular parameters of PPO, the angle $\phi_{SH} = \pi/4$ was found to be close to optimal in terms of enantioselectivity.

Figure 6 shows the projections of dipole moment along the laboratory $X$, $Y$, and $Z$ axes as functions of time. The two-color pulse induces orientation in the $X$ and $Y$ directions, and these orientations are the same for both enantiomers (see figures 6(a) and (b)). Moreover, figures 6(c) and (d) show the appearance of the dipole signal along the laser propagation axis ($Z$ axis), $\langle \mu_Z(t) \rangle$. $\langle \mu_Z(t) \rangle$ is enantioselective, namely it has an opposite sign for the two enantiomers. A similar type of orientation was predicted in the case of chiral molecules excited by THz pulses with twisted polarization [49]. In these cases, all three projections of the dipole moment, $\langle \mu_X \rangle$, $\langle \mu_Y \rangle$, $\langle \mu_Z \rangle$ are non-zero, and the projection along the field propagation direction is enantioselective. In contrast, laser pulses with twisted polarization induce (enantioselective) orientation only along the laser propagation direction [38–43]. As was shown in the cases of laser/THz pulses with twisted polarization, the time scale of polarization twisting should be comparable with that of the molecular rotation. In contrast, here the demonstrated enantioselective orientation is caused by a single impulsive excitation.

The analysis of the interaction potential shows that when $\phi_{SH} = \pi/4$, the field-hyperpolarizability interaction potentials of (R)-PPO and (S)-PPO molecules have a single global minimum at

$$M^{(R)} \simeq (0, 0.32\pi, 1.43\pi), \quad M^{(S)} \simeq (0, 0.68\pi, 1.57\pi).$$

The existence of a unique global minimum implies that, in principle, the chiral molecule can be fully oriented in space [74]. In addition,

$$U \left[ M^{(R)}_2 \right] \left[ \mu^{(R)} \right]^T \simeq (0.50, 0.62, -0.09)^T,$$

$$U \left[ M^{(S)}_2 \right] \left[ \mu^{(S)} \right]^T \simeq (0.50, 0.62, 0.09)^T,$$

where $\mu^{(S)}$ is the dipole moment vector of (S)-PPO molecule. This means that the two-color field kicks the dipole moment toward a certain direction in space, such that the dipole projections on all three laboratory axes $X$, $Y$, $Z$ are non-zero. The sign of the projection along the $Z$ direction is opposite for the two enantiomers, in agreement with the enantioselective orientation visible in figures 6(c) and (d).

In the case of non-chiral CH$_2$O and SO$_2$ molecules, $\langle \mu_2 \rangle = 0$ for all $\phi_{SH}$ (see equation (1)). As an example, we consider the CH$_2$O molecule and $\phi_{SH} = \pi/4$. The field-hyperpolarizability interaction potential has two minima at $M_1 \simeq (0.37\pi, \pi/2, \pi/2)$ and $M_2 \simeq (0.37\pi, \pi/2, 3\pi/2)$, such that

$$U(M_1)\mu^T = U(M_2)\mu^T \simeq (-0.38, -0.87, 0)^T,$$
which implies zero dipole orientation along the laser propagation direction.

5. Conclusions

We have investigated the orientation of asymmetric-top (including chiral) molecules excited by two-color femtosecond laser pulses. In the case of planar asymmetric-top molecules, including formaldehyde and sulfur dioxide, the excitation by an orthogonally polarized two-color pulse leads to the 3D orientation. The orientation direction can be controlled by the relative angle between the polarizations of the FW and the SH. The degree of orientation can be enhanced by optimizing the pulse parameters and by applying a sequence of multiple delayed pulses [5, 75–80]. The studied 3D molecular orientation may be useful e.g. in imaging of atomic motion using free-electron lasers and electron diffraction [81–83]. In addition, in the case of the formaldehyde molecule, the orientation lasts long after the end of the pulse. This long-lasting orientation of the dipole moment may, potentially, be probed by even-harmonic generation and may be useful for enhancing the deflection of molecular beams in the presence of inhomogeneous electrostatic fields [84]. Uniquely to chiral molecules, the induced orientation appears along the laser propagation direction when the polarizations of the FW and the SH are neither parallel nor orthogonal. Moreover, the sign of the orientation is opposite for the two enantiomers. This enantioselective orientation may be useful for ultra-fast enantiomeric excess analysis and potentially also for the eventual separation of the two enantiomers.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

Appendix A. Field-polarizability and field-hyperpolarizability interaction potentials

The external field vector \( \mathbf{E} \) can be expressed in the molecular reference frame with the help of the transformation matrix parametrized by the three Euler angles \( \phi, \theta, \chi \) (transpose of the matrix \( U \) in equation (B.1)). Accordingly, the interaction potential (see equation (5)) becomes a function of \( \phi, \theta, \chi \) as well. For the orthogonally polarized two-color pulse, after averaging over the optical cycle, the field-polarizability interaction of asymmetric-top molecule (CH\(_2\)O and SO\(_2\)) is given by

\[
V_\alpha = -\frac{e^2}{4} \left\{ \left[ \cos(\phi) \cos(\chi) \sin(\phi) \sin(\chi) \right]^2 \alpha_{bb} + \left[ \cos(\phi) \sin(\phi) \sin(\phi) \sin(\chi) \right]^2 \alpha_{cc} + \sin^2(\phi) \cos^2(\phi) \alpha_{aa} \right\}
\]

The field-hyperpolarizability interaction potentials of CH\(_2\)O and SO\(_2\), after averaging over the optical cycle, are given by

\[
V_\beta = -\frac{e^2}{64} \left\{ \left( 4 \sin(\phi) \sin(\phi) \left[ 6 \cos^2(\phi) \cos^2(\phi) \cos^2(\chi) - 1 \right] + 3 \cos(2\phi) \sin^2(\chi) \right) \beta_{abb} + \left( 4 \sin(\phi) \sin(\phi) \left[ 6 \cos^2(\phi) \cos^2(\phi) \sin^2(\chi) - 1 \right] + 3 \cos(2\phi) \cos^2(\chi) \right) \beta_{acc} + 8 \sin^2(\phi) \cos^2(\phi) \sin(\phi) \beta_{aaa} \right\}
\]

and

\[
V_\gamma = -\frac{e^2}{32} \left\{ \left[ \cos(\phi) \sin(\phi) \cos(\chi) + \cos(\phi) \sin(\phi) \right] \times \left[ \cos(\phi) \cos(\phi) \cos(\chi) - \sin(\phi) \sin(\phi) \right]^2 \beta_{bcb} + \left[ \cos(\phi) \sin(\phi) \sin(\phi) \cos(\chi) \right] \times \left[ 3 \cos^2(\phi) \sin(2\phi) \sin(2\phi) \right] \times 2 \left[ 1 + \cos(2\phi) \cos(2\phi) \sin(2\phi) \right] \beta_{bcc} + 2 \cos^2(\phi) \cos(\phi) \left[ 3 \cos(\phi) \sin(2\phi) \cos(\phi) \right] \times 3 \cos(2\phi) - 1 \right] \sin(\chi) \beta_{bab}, \right\}
\]

respectively.

Appendix B. The relation between laboratory and molecular frames

The relation between the laboratory and molecular frames is given by (\(X, Y, Z\)) \( = U(\phi, \theta, \chi)(b, c, a)^T\), where the transformation matrix reads
\[ U(\phi, \theta, \chi) = \begin{pmatrix}
\cos(\phi) \cos(\theta) \cos(\chi) - \sin(\phi) \sin(\chi) & -\cos(\phi) \cos(\theta) \sin(\chi) - \sin(\phi) \cos(\chi) & \cos(\phi) \sin(\theta) \\
\sin(\phi) \cos(\theta) \cos(\chi) + \cos(\phi) \sin(\chi) & \sin(\phi) \cos(\theta) \sin(\chi) + \cos(\phi) \cos(\chi) & -\sin(\phi) \sin(\theta) \\
-\sin(\theta) \cos(\chi) & -\sin(\theta) \sin(\chi) & \cos(\theta)
\end{pmatrix}. \] (B.1)
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