Rotational Control of Asymmetric Molecules: Dipole- versus Polarizability-Driven Rotational Dynamics

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We experimentally study the optical- and terahertz-induced rotational dynamics of asymmetric molecules in the gas phase. Terahertz and optical fields are identified as two distinct control handles over asymmetric molecules, as they couple to the rotational degrees of freedom via the molecular dipole and polarizability selectively. The distinction between those two rotational handles is highlighted by different types of quantum revivals observed in long-duration (>100 ps) field-free rotational evolution. The experimental results are in excellent agreement with random phase wave function (RPWF) simulations [Phys. Rev. A 91, 063420 (2015)] and provide verification of the RPWF as an efficient method for calculating asymmetric molecular dynamics at ambient temperatures, where exact calculation methods are practically not feasible. Our observations and analysis pave the way for orchestrated excitations by both optical and terahertz fields as complementary rotational handles that enable a plethora of new possibilities in three-dimensional rotational control of asymmetric molecules.

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Nonordered media such as gas, liquid, and most solid phases consist of a large number of molecules oriented in all possible directions. Such “isotropic” samples lack association between the molecular and laboratory frames, and thus their spectroscopic signals are inherently angularly averaged, impeding the extraction of molecular-frame-dependent observables. Motivated by lifting this angular averaging, vast efforts have been put into controlling molecular angular distributions in gas.

Most of these efforts have focused on molecular alignment in which the most polarizable molecular axes align with a chosen lab-frame axis. Recently, the interest is gradually shifting toward molecular orientation in which the permanent molecular dipoles point preferentially toward a chosen lab-frame direction (positive or negative lab z axis). Molecular orientation provides additional desirable features such as transiently lifted inversion symmetry that enables optical phenomena governed by even orders of the nonlinear susceptibility $\chi^{(2n)}$, like generation of even harmonics [1] and directional molecular ionization or dissociation [2]. Throughout the years, coherent rotational control has yielded tremendous progress in various tangential fields in addition to molecular frame spectroscopy [3–5].

Our aims in this work are threefold: to study and compare between optical- and terahertz-induced rotational dynamics in asymmetric molecules; to establish single-cycle terahertz (THz) fields as a dipole-selective rotational handle; and to experimentally verify the random phase wave function (RPWF) method as an efficient and reliable method for calculating rotational dynamics of asymmetric molecules at ambient temperatures.

Before delving into the dynamics of asymmetric tops, we note that the vast majority of ultrafast rotational control studies have focused on linear molecules and symmetric tops typically modeled as quantum mechanical rigid rotors with effectively only one moment of inertia. Such molecules show periodic recurrences manifested by anisotropic distributions with each revival time, given by $T_{rev} = 1/(2Bc)$ with $B$ the rotational coefficient in [cm$^{-1}$] and $c$ the speed of light [6,7]. Moreover, most of the efforts focused on inducing molecular alignment. Significantly fewer works focused on molecular orientation and even less on orientation of asymmetric molecules that are at the focus of this work. In addition to their complicated quantum rotational dynamics, asymmetric tops introduce highly demanding computational challenges [8–11].

Laser-induced rotations of asymmetric tops.—The theoretical and experimental foundations of asymmetric-top rotational dynamics have been laid by Felker [12] more than two decades ago and have been actively reinforced since [13–23]. Alignment of asymmetric tops has been achieved by elliptically polarized pulses [18] and multiple pulses with controlled polarizations [24]. Existing techniques for the orientation of asymmetric molecules rely on combinations of weak electrostatic fields (dc) and ultrashort laser pulses [25–27]; however, they require low rotational temperatures achieved via supersonic beam expansion and correspondingly low gas densities that prohibit all-optical detection such as birefringence measurements and high-harmonic generation. Field-free orientation has been demonstrated in linear molecules by either mixed-field ($\omega + 2\omega$) excitations [28,29] or single-cycle THz fields [30–34], both applicable to
ambient gas temperatures and high densities allowing all-optical probing.

Here we utilize intense THz fields as dipole-selective rotational handles of asymmetric molecules to induce orientation and rotational responses that are considerably different from those induced by optical pulses. We demonstrate THz- and optical-induced dynamics of sulfur dioxide (SO$_2$) molecules, serving as a model for asymmetric tops [10,11,35].

**Theoretical.**—Asymmetric tops like SO$_2$ are described by three different moments of inertia as shown in Fig. 1. The rotational Hamiltonian $\hat{H} = \hat{H}_0 + \hat{V}(t)$ includes $\hat{H}_0 = \hat{\mathbf{L}}^2/2I_a + \hat{\mathbf{L}}^2_b/2I_b + \hat{\mathbf{L}}^2_c/2I_c$, the field-free rotational energy, and $\hat{V}$, the interaction term of the molecule with the external field. We study the rotational dynamics, induced by two different excitation fields: an ultrashort near-IR (optical) pulse (FWHM $\sim$ 100 fs duration, $\omega_{\text{optical}} = 3.75 \times 10^{14}$ Hz) and a single-cycle THz field (FWHM $\sim$ 1 ps, $\omega_{\text{THz}} \sim 5 \times 10^{11}$ Hz).

An ultrashort optical pulse induces rotational dynamics via the anisotropic polarizability components of the molecule (Fig. 1). The interaction with a linearly polarized pulse is given by $\hat{V}_{\text{optical}} = -\frac{1}{2} e^2(t) [\alpha_{aa}\cos^2\theta_a + \alpha_{bb}\cos^2\theta_b + \alpha_{cc}\cos^2\theta_c]$ where $e(t)$ is the pulse field envelope, $\alpha_{ij}$ is the field component along the molecular frame $ii$ axis, and $\theta_i$ is the angle between the field polarization and the $ith$ molecular frame axis [10–12,15]. Thus, the main contribution to the rotational dynamics comes from the most polarizable axis, the O-O axis of SO$_2$ (see Fig. 1).

A single-cycle THz field spanning the 3–30 cm$^{-1}$ range interacts with the molecule via its permanent dipoles [31–34]. The interaction term $\hat{V}_{\text{THz}} = \frac{1}{2} \mathbf{b} \cdot \mathbf{E}(t)$ rotates the dipole axis ($b$ axis of SO$_2$; see Fig. 1) to orient in the direction of the THz field. Since the THz field oscillates at a much slower rate (≈750-fold slower) than the optical field, the molecular dipoles are able to follow the field and orient in its direction via resonant rotational excitation [31,36].

**RPWF simulation details.**—Simulating rotational dynamics of asymmetric tops is far more computationally demanding than linear or symmetric top molecules owing to the existence of three-coupled rotational degrees of freedom [8–11]. At ambient temperatures, the large number of thermally occupied states make exact calculation methods very costly and in many cases practically not feasible. Here we use the RPWF method, recently adopted by us for this purpose [9]. The initial state of the system is represented by a rotational wave function $|\theta_k\rangle = \sum_{JM_l} e^{-E_{JM_l}/k_B T} |Ze^{i\theta_{JM_l}}| JM_l$ with Boltzmann weighted magnitudes for the wave functions but with randomly chosen phases $\theta_{JM_l}$. Such an initial state contains coherences between the rotational states that should be absent from the thermal ensemble. With an increasing number of realizations ($k$), the randomly chosen phases and corresponding coherences cancel out due to destructive interferences, and the correct “coherence-free” representation of the initial thermal ensemble is achieved [37–40]. At later times throughout the quantum evolution, the RPWF maintains the correct dynamics due to quantum typicality [41]. We have recently shown [9] that the convergence efficiency of the RPWF method to exact calculations increases with the initial temperature of the ensemble and with the exciting field strength. The calculation of the optical-induced alignment of SO$_2$ is performed here by RPWF for the first time and provides yet another test bed for the integrity of the RPWF by comparison to experimental results (Fig. 2).

In accordance with the spin symmetry selection rules, only rotational levels that are symmetric with respect to the $b$ axis were taken into account. Taking the molecular dipole axis as the $z$ axis of the molecule following the textbook convention [43], only states with even $K$ participate in the calculation.

**Experimental.**—The rotational responses of SO$_2$ to the optical and the THz fields were measured separately in two different experimental setups: a time-resolved optical birefringence setup and time-resolved THz-induced emission measurements briefly described hereafter.

**Optical-induced birefringence in SO$_2$.**—The time-resolved birefringence of a 25 torr SO$_2$ gas sample at ambient temperature is shown in Fig. 2. The experimental setup is similar to that recently reported in Refs. [10,44] based on the weak-field polarization detection technique [42,45].

A 100 fs pulse is split to form an optical pump ($\sim$50 μJ/pulse, 800 nm) and a weak 400 nm probe (generated via SHG in a BBO crystal), linearly polarized 45° relative to the 800 nm pump. The pump and probe beams are recombined by a dichroic mirror to propagate collinearly in the sample cell. The diameter of the pump beam is reduced by an iris to assure complete overlap with the probe throughout the sample. Following their interaction with the pump, the molecules assume anisotropic angular distributions manifested as transient birefringence of the sample. The polarization changes of the probe due to its propagation in the birefringent sample are analyzed by a polarizer and a photodiode [46]. The experimental optical-induced birefringence setup is described in Supplemental Material, Sec. 1 [47].

The observed birefringence signal is given by $I_{\text{Signal}}(t) \propto \alpha_{aa} (\cos^2 \theta_a)(1/3) + \alpha_{bb} (\cos^2 \theta_b)(1/3) + \alpha_{cc} (\cos^2 \theta_c)(1/3)$, with contributions from all three

\[ \begin{align*}
\text{b-axis:} & \quad \mu = 1.62 \text{ Debye} \\
[2l_a] = B_a = 0.3442 \text{ cm}^{-1} \\
\alpha_{aa} = 20.8 \text{D} \\
\text{a-axis:} & \quad [2l_a] = B_a = 2.028 \text{ cm}^{-1} \\
\alpha_{aa} = 31.3 \text{D} \\
\text{c-axis:} & \quad [l_a] = B_a = 0.2935 \text{ cm}^{-1} \\
\alpha_{aa} = 18.6 \text{D}
\end{align*} \]

FIG. 1. Rotational coefficients and polarizability components along the three principal axes of the SO$_2$ molecule. The permanent dipole moment points along the $b$ axis.
molecular axes’ polarizabilities, $\alpha_{ii}$ (Fig. 1), weighted by the transient change in the alignment of the axes. The latter are given by the ensemble-averaged projections of the principal molecular axes onto the polarization axis of the pump pulse (laboratory $Z$ axis). $\langle \cos^2 \theta_i \rangle(t) - 1/3 \quad (i = a, b, c)$.

The optical-induced birefringence of SO$_2$ in Fig. 2 shows excellent agreement between the experimental (solid blue line) and the RPWF-simulated data (solid red line). The dynamics consists of mainly the $J$-type and $C$-type revivals [12], with periods of $[2(B_a + B_c)]^{-1} = 26.1$ ps and $[4B_a]^{-1} = 28.4$ ps, respectively. The weak birefringence oscillations observed starting from $t \sim 35$ ps are also perfectly captured by the RPWF simulation (shown in the orange dashed frame in Fig. 2), thereby providing clear validation of the RPWF method for rotational dynamics. Minor experimental deviations from the simulated signal are due to laser fluctuations and photodiode noise (as observed in the background signal around 15 ps < $t$ < 25 ps).

To examine the actual dynamics associated with these types of revivals, we present in Fig. 3 the transient alignment of the three principal molecular axes onto the $Z$-lab axis.

The $J$-type revivals involve the anisotropic distribution of all three molecular axes, with the molecular $b$ and $c$ axes antialigned at the instance of $a$-axis alignment and vice versa. This motion is driven via the most polarizable molecular axis ($a$ axis), forcing its alignment along the $Z$-lab axis, and hence entails the antialignment of the $b$ and $c$ axes (see $J$ revival cartoon in the Supplemental Material [47,48]). Correspondingly, the $J$-type revival period is given by $1/2[B_a + B_c]$, manifesting the rotation around the $b$ and $c$ molecular axes. Similarly, the $C$-type revivals describe rotation around the $c$ axis, with the $a$ axis aligned at the instance of $b$-axis antialignment and vice versa (see $C$ revival cartoon in the Supplemental Material [47,48]); hence, the $C$-type revival period is given by $1/[4B_a]$ and does not depend on the rotational coefficient of the $b$ axis ($B_b$). We note that another periodic feature, the $A$-type revivals with a period of $1/[4B_a] = 4.9$ ps, is captured by the simulation for axes $b$ and $c$ with opposite contributions from the two axes. However, due to very similar polarizabilities along the $b$ and $c$ axes, the weighted $A$-type signal is absent from the total alignment signal. (For a simulated alignment of the three molecular axes for the $A$-type revivals, see Supplemental Fig. 4 [47].)

FIG. 2. Experimental time-resolved birefringence (solid blue line) and RPWF-simulated alignment (solid red line) from a 25 torr SO$_2$ gas sample at ambient temperature, following excitation by a 100 fs optical pulse (800 nm). The $J$-type revivals (with a period of 26.1 ps) and the $C$-type revivals (period 28.4 ps) are marked in the figure. Note the alternating signal phases of the $J$-type with each revival and the constant phases of the $C$-type signals, shown in the green dashed insets for the first and second $J$-type and $C$-type revivals. The dashed orange inset depicts the weak oscillatory $C$-type and $J$-type signals at the 58–76 ps time frame, with close to perfect correspondence between the experimental and RPWF-simulated data. From the optical birefringence measurements, the degree of alignment at the peak of the first $J$-type revival is $\langle \cos^2 \theta_i \rangle(t) - 1/3 = 0.006$ [42] (corresponding to 0.25 in the arbitrary units of the birefringence axis). Significantly higher degrees of alignment are possible with higher intensities of the pump pulse, controlled pulse duration, and rotationally cold molecules [24].

THz-induced orientation of SO$_2$.—We now turn to THz-induced rotational dynamics of the SO$_2$ gas sample. The experimental setup used for THz-induced orientation measurements is a 4-f reflective setup similar to that used in Ref. [31] (for details see Supplemental Material, Sec. 2 [47]). An ultrashort laser pulse (100 fs, 800 nm) with 3.5 mJ pulse energy was used to generate a ~3-uJ single-cycle THz pulse by tilted pulse front optical rectification [49]. The THz pulse is focused by an off-axis parabolic reflector into the center of a 10 cm long static gas cell through a 10 mm wide polytetrafluoroethylene window. The THz beam is recollimated by an off-axis parabolic reflector at the output of the cell and focused onto a GaP crystal (0.5 mm thickness) for its electro-optic sampling (EOS) by a variably delayed optical readout pulse [50,51].

FIG. 3. RPWF-simulated alignment of the three principal molecular axes along the $Z$-lab axis $\langle \cos^2 \theta_i \rangle(t) - 1/3 \quad (i = a, b, c)$. In the observed signal, each axis is weighted by its polarizability; hence, the signal is dominated by the alignment of the (most polarizable) $a$ axis.

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Polar dipoles are preferentially oriented toward the angular distributions. At these events, the permanent molecular dipoles oscillate between the lab-frame direction giving rise to the creation and annihilation of a macroscopic dipole in the sample. These dipole oscillations manifest by electromagnetic field emission with a π phase relative to the driving field, much like a resonantly driven antenna. The polarization induced in an antenna is π/2 phase shifted relative to the driving field, and the field emitted by the antenna is yet another π/2 shifted relative to its polarization. In analogy, the transient orientation of the SO$_2$ dipoles is π/2 phase shifted relative to the THz field carrier-envelope phase [31], and the emitted THz burst is another π/2 shifted with respect to the orientation.

Figure 4 shows the time-resolved FID signal emitted from a 23 torr SO$_2$ sample at room temperature. The experimental (solid blue line) begins at $t \sim 5$ ps after the THz excitation due to the large amplitude differences in the obtained FID signal and the exciting THz field (peak value of 0.87 in the scale of Fig. 4). The RPWF-simulated signal (solid red curve) is generated by simulating the orientation of the sample throughout the entire time domain and introducing a π/2 phase shift as described above. The ensemble-averaged orientation is the projection of the dipole vector (positive $b$-axis direction in SO$_2$) onto the THz polarization axis (lab $Z$ axis), $\langle \cos \theta_b^{(0)} \rangle$. We note that the raw EOS signal obtained in the experiment consists of a large number of satellite signals emanating from various reflections of both the THz pump and optical probe pulses in the GaP crystal, the cell windows, and residual water vapor in the THz beam path outside the cell. In order to extract the SO$_2$ signal, we measured the response function of the system by EOS of the evacuated cell and used it to deconvolve the SO$_2$ signal from the raw EOS data (see Supplemental Material Sec. 3 [47] for details). While the extracted signal is in good agreement with the RPWF simulations, slight discrepancies remain and are attributed mainly to the not-perfect signal retrieval procedure used (see Supplemental Material Sec. 3 [47]) and in part to a water vapor FID signal due to incomplete dry air purging.

Despite the crowded oscillatory character of the SO$_2$ emission in Fig. 4, the fundamental revival features are clearly observed with a period of $|2B_b - B_h - B_c|^{-1} \sim 9.8$ ps corresponding to Felker’s hybrid-type revival [12]. The polarity of the signal alternates with the revival periods such that the phases at even recurrence signals are π shifted with respect to the odd ones (marked by “DHyb” for dipole-induced hybrid type revivals). The existence of the DHyb revivals as the main feature of Fig. 4(a) is apparent from its Fourier transform shown in Fig. 4(c) manifesting several peaks distant by 3.4 cm$^{-1} = 2B_a - B_h - B_c$. During the fundamental emission events (with a 9.8 ps period), the molecular dipoles preferentially point toward the positive or negative $z$-axis direction [see inset sketches DHyb(1) and DHyb(2) in Fig. 4(a)]. The DHyb revivals persist for a long time under field-free conditions, enabling additional laser interactions with the field-free oriented SO$_2$ samples for enhanced rotational control or nonlinear spectroscopic interrogation of the molecules in their molecular frame. Note that the periodic orientation revivals of Fig. 4 (with a 9.8 ps period) are absent from the alignment results of Fig. 2 and vice versa; the $J$-type (26.1 ps) and $C$-type (28.4 ps) revivals are absent from the THz-induced dynamics of Fig. 4. Namely, the THz and optical pulses induce distinct rotational dynamics in asymmetric SO$_2$ molecules and induce selective rotational motions due to the different nature of their interactions.

The transmitted THz field consists of quasiperiodic THz free-induction-decay (FID) bursts, emitted upon molecular orientation governed by the rotational dynamics of the excited gas. The FID emission profile follows the gradient of the time-dependent orientation [31] and is explained here by classical electrodynamics: Subsequent to their dipole-induced rotation, the SO$_2$ molecules exhibit transiently squeezed angular distributions. At these events, the permanent molecular dipoles are preferentially oriented toward the $+Z$ (or $-Z$) lab-frame direction giving rise to the creation and annihilation of a macroscopic dipole in the sample. These dipole oscillations manifest by electromagnetic field emission with a π phase relative to the driving field, much like a resonantly driven antenna. The polarization induced in an antenna is π/2 phase shifted relative to the driving field, and the field emitted by the antenna is yet another π/2 shifted relative to its polarization. In analogy, the transient orientation of the SO$_2$ vapor in the THz beam path outside the cell. In order to extract the SO$_2$ signal, we measured the response function of the system by EOS of the evacuated cell and used it to deconvolve the SO$_2$ signal from the raw EOS data (see Supplemental Material Sec. 3 [47] for details). While the extracted signal is in good agreement with the RPWF simulations, slight discrepancies remain and are attributed mainly to the not-perfect signal retrieval procedure used (see Supplemental Material Sec. 3 [47]) and in part to a water vapor FID signal due to incomplete dry air purging.

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mediated via the permanent dipole and the anisotropic polarizability, respectively.

Conclusions.—Unlike linear and symmetric top molecules, that have their dipole axis and the most polarizable axis parallel to each other, in SO$_2$, as in most asymmetric molecules, the dipole and the most polarizable axes are not parallel to one another (in SO$_2$ they are situated perpendicularly). This manifests in distinctively different dynamics induced by either THz or optical fields, thereby providing two distinct handles for controlling rotational dynamics in asymmetric molecules. Well-concerted utilization of these handles paves a path to realizing three-dimensional control over molecular angular distributions, achieving much higher degrees of orientation in rotationally cold molecular ensembles [34], inducing torsion in molecules, and can aid in breaking down congested rotational dynamics by associating the rotational responses induced by THz and optical fields separately to their molecular-frame handles. Coapplication of THz and optical rotational handles can significantly extend the currently available rotational control playground to yield novel rotational responses and dynamics unreachable by either of these fields alone.

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Unlike the balanced detection of Refs. [10,44], we record only one channel of time-resolved transmission through the analyzing polarizer, which was found to provide a sufficient S/N ratio required for our measurement.

See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.117.103001 for description of the experimental setups used in the work (Secs. SI.1 and SI.2), a description of the deconvolution scheme used for retrieving the THz-induced signals (Sec. SI.3) and a simulation result of the A-type revivals (Sec. SI.4). In addition, the Supplemental Material includes two movie files with short cartoons of the rotational dynamics at the J and C revivals.

We note that the molecular angular distributions shown in the short cartoons are plotted for the extreme cases of “close to perfect” alignment of the molecular axes under consideration and do not represent the actual degree of alignment achieved in the experiment.

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