Echo-enhanced molecular orientation at high temperatures

Iliya Tutunnikov,1,∗ Long Xu,1,† Yehiam Prior,1,‡ and Ilya Sh. Averbukh1,†
1AMOS and Department of Chemical and Biological Physics,
The Weizmann Institute of Science, Rehovot 7610001, Israel
(Dated: July 19, 2022)

Ultrashort laser pulses are widely used for transient field-free molecular orientation – a phenomenon important in chemical reaction dynamics, ultrafast molecular imaging, high harmonics generation, and attosecond science. However, significant molecular orientation usually requires rotationally cold molecules, like in rarefied molecular beams, because chaotic thermal motion is detrimental to the orientation process. Here we propose to use the mechanism of the echo phenomenon previously observed in hadron accelerators, free-electron lasers, and laser-excited molecules to overcome the destructive thermal effects and achieve efficient field-free molecular orientation at high temperatures. In our scheme, a linearly polarized short laser pulse transforms a broad thermal distribution in the molecular rotational phase space into many separated narrow filaments due to the nonlinear phase mixing during the post-pulse free evolution. Molecular subgroups belonging to individual filaments have much-reduced dispersion of angular velocities. They are rotationally cold, and a subsequent moderate terahertz (THz) pulse can easily orient them. The overall enhanced orientation of the molecular gas is achieved with some delay, in the course of the echo process combining the contributions of different filaments. Our results demonstrate that the echo-enhanced orientation is an order of magnitude higher than that of the THz pulse alone. The mechanism is robust – it applies to different types of molecules, and the degree of orientation is relatively insensitive to the temperature. The laser and THz pulses used in the scheme are readily available, allowing quick experimental demonstration and testing in various applications. Breaking the phase space to individual filaments to overcome hindering thermal conditions may find a wide range of applications beyond molecular orientation.

I. INTRODUCTION

Control over the absolute orientation of molecules in space is essential for a wide variety of physical and chemical processes such as ultra-fast structural imaging, photon-induced processes, or chemical reactions [1–6]. Diverse optical methods have been developed to align and orient molecules in the gas phase under field-free conditions. A well-established route for orienting polar molecules is combining intense non-resonant laser fields with weak electrostatic fields [7–16]; another one involves using intense two-color laser pulses to induce molecular orientation via interaction with the molecular hyperpolarizability [17–31]. For chiral molecules, it is possible to induce orientation by using laser pulses with twisted polarization [32–38]. With the advance in terahertz (THz) technology, it has become possible to orient polar molecules using single- or half-cycle THz pulses through coupling to the permanent molecular dipole moment [39–49].

The efficiency of the above-mentioned methodologies deteriorates fast with increasing rotational temperature, and the molecular orientation is typically just a few percent at room temperature — too low for many practical applications. High temperature is detrimental to efficient orientation due to the increased dispersion of the molecular angular velocities with temperature. In laser-based methods, the degree of orientation may be enhanced by simply increasing the field intensity. Still, this approach has a practical limit because high-intensity laser pulses, especially two-color fields, give rise to significant molecular ionization, an undesired consequence of the strong field. On the other hand, in the case of THz pulses, the available field strengths are insufficient for achieving a sizable degree of orientation. Thus, attaining efficient molecular orientation at room temperatures is still an open, very challenging problem.

Over the years, several sophisticated proposals for enhancing molecular alignment and orientation have been put forward. These include applying optimized sequences of pulses [50–54], optimizing pulses’ parameters [55–64], and combining one-color laser pulses with two-color and THz pulses [65–74]. Several schemes were experimentally implemented [43, 75–77] and demonstrated improved orientation, mainly in the low-temperature regime.

Here, we propose an efficient and general approach for achieving significant field-free molecular orientation by moderate THz pulses even at room temperature. The method uses a pair of time-delayed pulses arranged in the echo configuration. The first, non-resonant laser pulse transforms a broad and smooth thermal probability-density distribution in the molecular rotational phase-space into multiple filaments (narrow strips). The second (typically weak) delayed THz excitation is then applied to the “filamented” molecular ensemble and causes a significant orientation of molecular groups belonging to different narrow filaments, each evolving independently. The enhanced ensemble-averaged orientation is achieved after some additional delay when the contributions of the independent filaments come together by the mechanism of echo formation. We show that for a proper choice of the excitation parameters, the amplitude of the orientation echo may be an order of magnitude higher than the orientation produced by the THz pulse alone. Moreover, the “filamenting” prepulse suppresses the detrimental effect of the molecular thermal rotational motion, making the echo amplitude rather insensitive to elevated temperatures.

Echoes are known in various domains of physics. The most notable example is Hahn’s spin-echo [78, 79] induced by two delayed magnetic field pulses. They result in a delayed magnetization response appearing after an additional delay equals the delay between the pulses. Various types of echoes have been discovered and studied in other fields, including photon echoes [80, 81], neutron spin-echo [82], cyclotron echoes [83], plasma-wave echoes [84], echoes in optically trapped cold atoms [85–87], echoes in particle accelerators [88–91], and echoes in free-electron lasers [92]. In addition, echoes in single quantum systems have been discussed [93, 94] and observed [95–97].
The enhancement mechanism of the present paper is related to the recently predicted and observed molecular alignment echoes [6, 98–108]. In contrast to the spin echoes [78, 79], they are based on the phenomenon of phase space filamentation known in non-linear systems, e.g., in the dynamics of stellar systems [109] and in accelerator physics [88, 90, 110]. Our paper presents the first application of the filamentation-based echoes to the problem of molecular orientation.

The paper is organized as follows. We begin with a qualitative physical description of the scheme using a simplified model of rigid planar rotors. Then we present the results of three-dimensional classical and fully quantum simulations of the echo-enhanced orientation of linear and symmetric-top molecules at room temperature. Finally, we summarize the results and discuss the prospects of the proposed scheme.

II. QUALITATIVE DISCUSSION

To understand the physical principles behind the enhanced orientation, we start with a simplified planar rotor model, where a linear polar molecule is modeled as a rigid rotor restricted to rotate in the XY plane. To begin with, let us first consider the orientation dynamics induced by a single orienting kick. The orienting interaction potential is \( \propto -\cos(\theta) \), where \( \theta \) is the angle between the molecular axis and the X-axis. Such a potential describes, e.g., the interaction of a single- or half-cycle THz pulse with the permanent molecular dipole.

**Single orienting kick** — In the impulsive approximation (when the change in \( \theta \) during the pulse is negligible), \( \theta \) and the molecule’s angular velocity, \( \omega \) after the orienting kick are given by

\[
\theta(t) = \theta_0 + \omega t; \quad \omega = \omega_0 - P_{or} \sin(\theta_0),
\]

where \( \theta_0 \) and \( \omega_0 \) are the initial angle and angular velocity, \( P_{or} \) is proportional to the amplitude of the orienting field, \( \varepsilon_{0,or} \) [for details, see Appendix A, Eq. (A5)] and has a physical meaning of the molecular angular velocity change due to the kick.

To study the rotational dynamics of an ideal molecular gas, we consider a collection of planar rotors that are initially isotropically distributed in the XY plane. At zero initial temperature, the phase space density before the kick is presented by a horizontal line \( \omega = 0 \) (see Fig. 1, \( t = 0_+ \)). The orienting pulse transforms the initial distribution into a saw-tooth line \( t = 0_+ \). With time, the curve folds as particles with opposite angular velocities move in opposite directions along the \( \theta \) axis. The ensemble-averaged degree of orientation, or the orientation factor \( \langle \cos(\theta) \rangle \) reaches a universal maximum \( \approx 58\% \), independent of \( P_{or} \) at \( t = 1.8/P_{or} \).

At finite, non-zero initial rotational temperature, the initial phase space density is given by \( p(\theta, \omega, t = 0) = (2\pi)^{-1/2}\sigma_T^{-1} \exp[-\omega^2/2\sigma_T^2] \), see Fig. 2(a). The parameter \( \sigma_T = \sqrt{k_B T/\hbar} \) defines the thermal dispersion of angular velocities, where \( T \) is the temperature, \( k_B \) is the Boltzmann constant and \( I \) is the moment of inertia of a single molecule. In the case of the initial thermal ensemble, the maximum degree of orientation is determined by the ratio \( P_{or}/\sigma_T \propto \varepsilon_{0,or}/\sqrt{T} \). When the orienting kick is relatively strong (or, equivalently, the temperature is relatively low), the resulting orientation is high, and vice versa, when the kick strength is insufficient to overcome the thermal dispersion of angular velocities. The orientation factor after the kick is given by [for derivation, see Appendix B1, Eq. (B5)]

\[
\langle \cos(\theta) \rangle (t) = e^{-\sigma_T^2 t^2/2} J_1(P_{or} t),
\]

where \( J_1(z) \) is the Bessel function of order one. When time is measured in units of \( 1/\sigma_T \), the orientation factor depends on the parameter \( P_{or}/\sigma_T \). Unfortunately, the currently available THz pulses result in a weak deformation of the phase space density at room temperature. Shortly after a typical orienting kick, the phase space density is delocalized and looks like in Fig. 2(b). When the orienting kick is relatively strong (or, equivalently, the temperature is relatively low), the phase space distribution folds like in Fig. 2(c).

**Phase space filamentation** — To help a weak orienting pulse overcome the detrimental effect of high temperatures, we suggest stratifying the rotational phase space density into numerous separated strips (filaments). This way, the orienting pulse interacts with many individual molecules.
narrow filaments rather than a single broadly dispersed thermal distribution. For stratification, we use a relatively strong prepulse – a nonresonant linearly polarized short laser pulse that precedes the orienting one. Intense laser pulses interacting with molecular polarizability have been widely used for inducing transient field-free molecular alignment [1−5]. However, we are not interested in the alignment effect but focus on the post-alignment stage characterized by highly stratified rotational phase space density [98, 100, 101] (see below).

A prepulse applied at \( t = 0 \) transforms the rotors variables according to

\[
\theta(t) = \theta_0 + \omega t; \quad \omega = \omega_0 - P_{\text{pre}} \sin(2\theta_0),
\]

where \( P_{\text{pre}} \) is proportional to the intensity of the laser prepulse [for details, see Appendix A, Eq. (A9)]. The phase space density after the prepulse is described by

\[
p(\theta, \omega, t) = \frac{\sigma T}{(2\pi)^{3/2}} \exp \left[ -\frac{\left( \omega + \frac{P_{\text{pre}} \sin(2\theta - 2\omega(t))}{2\sigma T} \right)^2}{2}\right],
\]

where we used Eq. (3) to express \( \omega_0 \) in terms of \( \omega \) and \( \theta \) after the pulse, and substituted \( \omega_0 \) into the Boltzmann distribution. The stratifying pulse imparts a sinusoidal shape on the phase-space density which folds with time. Shortly after the excitation, the phase-space distribution concentrates near \( \theta = 0, \pi \), corresponding to alignment along the X axis [see Fig. 3(a)]. It’s important for our discussion that with time, the phase space density undergoes filamentation and turns into a series of almost parallel filaments (strips) separated in angular velocity by \( \pi/t \) [see Eq. (4)]. Note that longer waiting times result in narrower filaments because the phase space volume is conserved.

After a delay \( \tau \) (at \( t = \tau \)), when the filaments are numerous and thin, [see Fig. 3(b)], we apply the orienting THz kick. Now, each filament resembles the phase-space density of an isotropic cold molecular ensemble (see Fig. 1, \( t = 0 \)). Moreover, since the dispersion of angular velocities within each filament is much smaller than the initial thermal dispersion, the interaction with the weak orienting pulse results in non-negligible deformation of the filaments (see Fig. 3(c)).

With time, each filament folds like in Fig. 2(c) developing a bunch. This folding does not result in substantial orientation just after the orienting kick because the bunches move relative to each other (they are spaced apart by \( \pi/\tau \) along the \( \omega \) axis). Due to the “quasi-quantization” of the angular velocities, the folded filaments synchronize near \( \theta = 0, \pi \) after an additional time delay equal to \( \tau \) (at \( t = 2\tau \), not shown). This synchronization manifests itself in alignment echo [6, 98−101, 107]. Similar synchronization dynamics is behind the echo phenomenon in several other nonlinear systems [88, 90, 93, 94, 97, 111].

After an additional delay of \( \tau \) (at \( t \approx 3\tau \)), we witness another echo, and this is a new observation. Each bunch re-synchronize in an asymmetric manner resulting in molecular orientation. First, the bunches accumulate near \( \theta = 0 \) [just before \( t = 3\tau \), see Fig. 3(d)], and then near \( \theta = \pi \) [just after \( t = 3\tau \), not shown]. The closeups in Fig. 3(d) demonstrate that the bunches in each filament look similar to those seen in Fig. 2(c). Such re-synchronizations happen again at later times: \( t = 5\tau, 7\tau, \ldots \), and manifest themselves in orientation echoes of higher orders.

\[
\langle \cos(\theta) \rangle(t) = \Theta(t - \tau) \sum_{\text{odd } k} S_k(t),
\]

where \( \Theta(t - \tau) \) is the step-function and

\[
S_k(t) = e^{-\sigma^2_j(t - k\tau)^2/2} J_k[P_{\text{pre}}(t - \tau)]J_{k-1}[P_{\text{pre}}(k\tau - t)].
\]

The orientation signal consists of a series of pulsed responses separated in time by \( 2\tau \). The first orientation echo (\( k = 3 \)) is proportional to

\[
S_3(t) \approx e^{-\sigma^2_j(t - 3\tau)^2/2} J_3(2P_{\text{pre}}\tau) J_2[P_{\text{pre}}(3\tau - t)].
\]

Here we used the facts that \( J_3(z) \) increases with \( z \) for \( z < 4 \), and \( t - 3\tau \) is relatively small (due to the Gaussian
FIG. 4. Orientation factor following combined excitation by stratifying and orienting pulses. Here, $P_{\text{pre}} = 2\sigma_T$, $P_{\text{rev}} = 0.1\sigma_T$. Note the enhanced orientation at $t = 2\tau$ for both cases of $\tau = 10/\sigma_T$ and $\tau = 20/\sigma_T$, with the higher degree of orientation for the longer delay. With the orienting pulse alone, the maximal orientation factor is $\approx 0.03$.

FIG. 5. Maximum orientation factor (absolute value) as a function of $P_{\text{pre}}$, for fixed $P_{\text{rev}} = 0.1/\sigma_T$. Note that for the low intensity prepulses, the degree of orientation is lower than in the absence of a prepulse altogether. This is a result of very minimal filamentation caused by the weak prepulses, which, in effect, slightly increases the dispersion of rotational velocities.

To illustrate this point, we consider the dynamics of a kicked quantum rigid 2D rotor (for details, see Appendix C). The rotational revival time of the quantum planar rotor is $T_{\text{rev}} = 4\pi I/\hbar$, where $I$ is the moment of inertia. Figure 6 shows the orientation factor in the quantum model in the presence of the stratifying (pre-pulse) and orienting kicks. Here, for demonstration purposes, we choose a short time delay $\tau = 0.025T_{\text{rev}}$, resulting in a relatively weak classical orientation echo at $t = 3/\sigma_T$. The amplitude of the classical echo is comparable to the maximal orientation obtained when using the orienting pulse alone, $\approx 3\%$. In striking contrast, a quantum echo emerges at a delay $-2\tau$ before the revival, at $t = 0.975T_{\text{rev}}$ with a much higher amplitude of $\approx 22\%$. Notice that echoes of the same magnitude (but opposite sign) emerge just before the half revival. Alignment echoes emerging before the quantum revivals, the so-called imaginary echoes, were studied by us both theoretically and experimentally [100, 101].

III. THREE-DIMENSIONAL SIMULATIONS

A. Numerical methods

So far, we considered the orientation enhancement in the simplified model of 2D rigid rotors. In this section, we apply the developed understanding to “real world” by considering the corresponding three-dimensional classical and quantum dynamics of linear and prolate symmetric-top molecules driven by the experimentally available laser and THz fields. The rotational dynamics is treated within the rigid rotor approximation. We model the time-dependent electric field, consisting of the delayed non-

between echoes and revivals needs to be taken into account. As was shown previously [87, 93], a particular type of echo exists, termed quantum echo. A series of quantum echoes emerge on a long time scale just before the quantum revivals. These echoes have a valuable property – in the limit of weak echo-inducing excitation (the orienting kick in our case), their amplitude is higher than the classical echoes discussed. We take advantage of this to achieve even higher molecular orientation with constrained delays.
resonant laser and single-cycle THz pulses, using
\[ E(t) = \varepsilon_{lsr}(t) \cos(\omega t) e_Z + \varepsilon_{THz}(t - \tau) e_Z, \tag{8} \]
where \( \omega \) is the carrier frequency of the laser pulse, \( \varepsilon_{lsr}(t) = \varepsilon_{0,lsr} \exp[-2 \ln 2 (t/\sigma_{lsr})^2] \), \( \varepsilon_{0,lsr} \) is the peak amplitude, and \( \sigma_{lsr} \) is the full width at half maximum (FWHM) of the laser pulse intensity profile. \( \varepsilon_{THz}(t) = \varepsilon_{0,THz}(1 - 2\kappa t^2) \exp(-\kappa t^2) \) [45, 46], where \( \varepsilon_{0,THz} \) is the peak amplitude of the THz pulse, \( \kappa \) determines the temporal width of the THz pulse. \( \tau \) is the time delay between the laser and THz pulses and \( e_Z \) is a unit vector along the laboratory \( Z \) axis. Figure 7 shows the electric field amplitude of the THz pulse as a function of time.

Classical simulation – We use the Monte Carlo method to simulate the behavior of a classical ensemble. Initially, \( N = 10^7 \) sample molecules are isotropically distributed in space. Their angular velocities are given by the Boltzmann distribution \( P(\Omega) \propto \exp[-I(\Omega^2)/(2k_B T)] \), where \( i = x, y, z \) refers to the molecular principal axes of inertia. In the case of a linear molecule \( I_x = I_y = I, I_z < I_x = I_y \equiv I \). For each sample molecule, the rotational dynamics in the rotating molecular frame is described by Euler’s equations [114]

\[ \dot{\mathbf{I}} = (\mathbf{I} \times \mathbf{\Omega}) + \mathbf{T}, \tag{9} \]
where \( \mathbf{I} = \text{diag}(I_x, I_y, I_z) \) is the moment of inertia tensor, \( \mathbf{\Omega} = (\Omega_x, \Omega_y, \Omega_z) \) is the angular velocity, and \( \mathbf{T} = (T_x, T_y, T_z) \) is the torque due to the interactions with the external electric field. The laser field interacts with the molecular polarizability \( \alpha = \text{diag}(\alpha_{xx}, \alpha_{yy}, \alpha_{zz}) \), and the torque is given by \( \mathbf{T} = [\alpha \mathbf{E}_{\text{mod}}(t)] \times \mathbf{E}_{\text{mod}}(t) \). The THz field interacts with the molecular permanent dipole moment, \( \mu \), and the torque is given by \( \mathbf{T} = \mu \times \mathbf{E}_{\text{mod}}(t) \). Here, \( \mathbf{E}_{\text{mod}}(t) \) is the representation of the electric field vector in the basis of the molecular principal axes. The relation between the laboratory and the rotating molecular frames is parametrized by a quaternion, \( \hat{q} = (q_0, q_1, q_2, q_3) \) [115, 116]. The quaternion’s equation of motion is \( \dot{\hat{q}} = \hat{q} \Omega / 2 \), where the quaternions multiplication rule is assumed, and \( \mathbf{\Omega} = (\Omega_x, \Omega_y, \Omega_z) \). The orientation factor at time \( t \) is obtained by averaging over all sample molecules (ensemble average). A more detailed description of the classical simulations can be found in [31, 36].

Quantum simulation – The Hamiltonian describing the rotational dynamics in the presence of external fields [see Eq. (8)] is [5, 117]
\[ H(t) = H_r + \mu \varepsilon_{THz}(t) \cos(\theta) - \frac{\Delta \alpha}{2} \varepsilon_{lsr}(t) \cos^2(\theta), \tag{10} \]
where \( H_r \) is the rotational kinetic energy Hamiltonian, \( \mu = |\mu| \) is the permanent molecular dipole moment, \( \Delta \alpha = \alpha_{zz} - \alpha_{xx} = \alpha_{zz} - \alpha_{yy} \) is the polarizability anisotropy, and \( \theta \) is the polar angle between the molecular symmetry axis and the laboratory \( Z \) axis (field polarization axis). The polarizability interaction term is averaged over the optical cycle.

In the simulations, the wave function \( \Psi \) is expressed in the basis of the eigenfunctions of \( H_r \). For a linear molecule, these are the spherical harmonics \( Y_{JM}^\alpha(\theta, \phi) \) (\( \phi \) is the azimuthal angle), while for a symmetric-top molecule, these are Wigner D-functions \( D_{JKM}^I(\theta, \phi, \chi) \), where \( \chi \) is the angle of rotation about the molecular symmetry axis. The quantum numbers \( J, M \) and \( K \) correspond to the magnitude of the angular momentum, projection of angular momentum on the laboratory \( Z \) axis, and projection of the angular momentum on the molecular symmetry axis. The eigenenergies are \( E_J = BJ(J + 1) \) (linear molecule) and \( E_{JK} = CJ(J + 1) + (A - C)K^2 \) (symmetric-top molecule), where \( B = \hbar^2/(2I) \) and \( A = \hbar^2/(2I_z) \). The time-dependent Schrödinger equation is solved by numerical exponentiation of the Hamiltonian matrix (see Exopík [118]).

In the case of the linear molecule, the orientation factor is given by the averaged expectation value
\[ \langle \cos(\theta) \rangle(t) = \frac{1}{Z} \sum_{JM} \langle \cos(\theta) \rangle_{JM}(t) e^{-E_J/(k_B T)}, \tag{11} \]
where \( Z \) is the partition sum, \( \langle \cos(\theta) \rangle_{JM}(t) = \langle \Psi_{JM}(t) | \cos(\theta) | \Psi_{JM}(t) \rangle \) for the initial state \( \Psi_{JM}(t) = 0 = Y_J^M, \) and the sum runs over all the thermally populated eigenstates \( Y_J^M \).

In the case of symmetric-top molecules, due to the increased number of thermally populated states, we use the random phase wave functions method (see, e.g. [119]) to simulate the behavior of the thermal ensemble. The orientation factor is given by the average
\[ \langle \cos(\theta) \rangle(t) = \frac{1}{N} \sum_{n=1}^N \langle \cos(\theta) \rangle_n(t), \tag{12} \]
where \( N \) is the number of initial states used, \( \langle \cos(\theta) \rangle_n(t) \) is the orientation factor obtained for the initial state \( \psi_n \)
\[ \psi_n = \sum_{JKM} \sqrt{\epsilon_K e^{-E_J/(k_B T)}} D_{JKM}^I \phi_{n,JKM} e^{i\varphi_{n,JKM}}, \tag{13} \]
where \( \varphi_{n,JKM} \in [0, 2\pi) \) is a random number and the sum runs over all the thermally populated eigenstates \( D_{JKM}^I \). For CH₃I molecule, the statistical weight due to the nuclear spin statistics is given by [120]
\[ \epsilon_K = \frac{(2I_H + 1)^3}{3} \left[ 1 + \frac{2 \cos(2\pi K/3)}{(2I_H + 1)^2} \right], \tag{14} \]
with \( I_H = 1/2 \).

B. Results: linear molecule

We consider OCS as an example linear molecule. The molecular properties were taken from NIST (DFT, method: CAM-B3LYP/aug-cc-pVTZ) [121]: \( I = 83.021 \text{ amu} \cdot \text{Å}^2, \mu = 0.755 \text{ Debye}, \) and \( \Delta \alpha = 3.738 \text{ Å}^3 \).
The rotational revival time of the OCS molecule is \( T_{\text{rev}} = 1/(2cB) \approx 82.4 \text{ps} \), where \( c \) is the speed of light.

Figure 8 shows the time-dependent orientation factor, \( \langle \cos(\theta) \rangle(t) \) obtained using classical and quantum simulations. The molecules were excited by the delayed laser and THz pulses [see Eq. (8)] at different initial rotational temperatures. The delay between the pulses was set to \( \tau = 7 \text{ps} \). The peak intensity of the laser pulse is \( I_{0,\text{laser}} = 4 \times 10^{13} \text{W/cm}^2 \), FWHM is \( \sigma_{\text{laser}} = 100 \text{fs} \). The THz pulse parameters are \( \varepsilon_{0,\text{THz}} = 1.0 \text{MV/cm} \), \( \kappa = 3.06 \text{ps}^{-2} \). Laser and THz pulses with similar parameters are readily available nowadays [122–125].

Both quantum and classical simulations demonstrate an immediate orientation response emerging during and shortly after the THz pulse excitation (at \( t \approx 7 \text{ps} \)). The first classical echo appears with a delay \( 2\tau \) after the THz pulse, at \( t \approx 21 \text{ps} \). The quantum mechanical result shows a strong echo signal before the orientation quantum revival, at \( t \approx 75.4 \text{ps} \). The magnitude of this echo is an order of magnitude larger than the maximum orientation induced by THz pulse alone. In agreement with the previous studies [87, 93] and the qualitative analysis based on the simplified models (see Sec. II), the orientation during the quantum echo is significantly higher compared to

The orientation during the classical echo. The magnitude of the quantum echo dominates at all temperatures represented in Fig. 8, including the room temperature, see Fig. 8(c).

Remarkably, the echo amplitude weakly depends on temperature (in the presented temperature range). This behavior can be understood with the help of the simplified model introduced in Sec. II. The laser pulse is intense enough to induce efficient phase-space filamentation at all the represented temperatures. With time, the number of filaments grows, and they become thinner. As a result, each molecular subgroup forming a single filament has much reduced dispersion of angular velocities (caused by chaotic thermal motion), and it is effectively “cold”. Instead of competing with the highly dispersed angular velocities of the initial thermal ensemble, the weak THz pulse competes against the cold narrow filaments. When the change of the rotation velocity due to the orienting pulse exceeds the width of the cold filaments, the following orientation echo dynamics becomes insensitive to this width, and, hence, to the initial molecular temperature.

As noted in the caption of Fig. 8 with the actual THz
pulses used here, the dependence of the maximal orientation obtained using the THz pulse only is counterintuitive, namely, the maximal orientation factor slightly increases with temperature instead of decreasing. This is in contrast to the case of impulsive orienting kicks considered in Sec. II. For relatively long THz pulses, the frequency contents of the pulse match the transitions between higher rotational levels and therefore is more effective in orienting higher temperature ensembles. A similar non-trivial behavior was studied theoretically in [126]. The dependence of orientation echoes on the pulse duration and other parameters will be elaborated further in a forthcoming publication.

As discussed in Sec. II, the echo amplitude increases with the time delay between the stratifying and orienting pulses (for fixed temperature and field parameters). Figure 9 shows the maximum orientation during the first classical echo [at delay 2τ after the THz pulse, see panel (a)] and during the quantum echo [at delay −2τ before the orientation revival, see panel (b)] for relatively short delays τ. For τ < 15 ps, the magnitude of both types of orientation echoes increases with τ, which is consistent with the qualitative discussion in Sec. II. Figure 9(a) shows good correspondence between the quantum and classical results for τ < 9. For longer delays, the curves diverge. At the local maximum in Fig. 9(b) (τ ≈ 9 ps), the enhanced (due to the prepulse) degree of orientation is an order of magnitude higher compared to the case of THz pulse alone. Figure 9(c) shows the global orientation maximum for various τ. The dependence on τ is periodic, and the period equal to half revival, T_{rev}/2 ≈ 41.2 ps. When τ ≈ T_{rev}/4, the maximum degree of orientation exhibits high-amplitude oscillations. The reason for this high sensitivity is the coalescence of the echo that appears after the THz pulse at τ ≈ 3τ = 3T_{rev}/4 and the echo that appears before the quantum revival at τ ≈ T_{rev} − τ = 3T_{rev}/4. Notice, the orientation can be further enhanced using a stronger prepulse (see Fig. 5 in Sec. II).

Previously, related schemes for enhancing the THz- and two-color-induced orientation were applied to cold OCS molecules (at 2 K in [43], and at 25 K in [77]). The orientation was substantially enhanced with the help of an aligning laser pulse. The delay between the aligning and orienting pulses was set to T_{rev}/4. The authors explained the enhancements using quantum mechanical arguments.

C. Results: symmetric-top molecule

To demonstrate the robustness of the proposed orientation enhancement mechanism, we consider an addition example molecule CH_3I that belongs to the class of symmetric-top molecules. The molecular properties were taken from NIST (DFT, method: CAM-B3LYP/cc-pVTZ-PP) [121]: I_x = I_y = I_z = 68.527 amu Å^2, I_2 = 3.23 amu Å^2, μ = 1.697 Debye, and Δν = 2.951 Å^3.

Figure 10 shows the orientation factor obtained using the quantum simulation at room temperature. The delay between the pulses was set to τ = 9 ps [see Eq. (8)]. All the parameters are the same as in Fig. 8, except the lower peak amplitude of the THz pulse, ε_{0,THz} = 0.3 MV/cm. On the short time scale, the quantum and classical results are close. The maximum orientation emerges before the quantum revival (during the quantum echo). The maximum orientation obtained using the THz pulse alone at room temperature is ten times lower, ≈ 1.6%.

IV. CONCLUSION

In this work, we introduced an echo-based approach for enhancing the field-free molecular orientation induced by THz pulses at high temperatures. The enhancement mechanism relies on the general nonlinear phenomenon of phase space filamentation and requires a single additional non-resonant laser pulse before the orienting THz excitation. The intense laser pulse effectively eliminates the detrimental thermal broadening by producing multiple separated narrow filaments in the molecular rotational phase space. Molecular subgroups forming individual filaments are effectively cold and easy to orient. The overall significant orientation of the whole ensemble is achieved in the course of echoes forming at set time delays. The various echoes emerging from the combined laser and THz excitation are qualitatively explained using the transparent and intuitive 2D model. In particular, we show that of many echoes possible, the so-called quantum echo, gives rise to the especially pronounced orientation enhancement. In the examples presented in the paper, the maximum orientation at room temperature reaches ~ 20%. With prepulses of higher intensity and various optimization procedures, even higher orientation can be expected. We demonstrate the robustness of the proposed scheme by using fully quantum simulations of the dynamics of linear (OCS) and symmetric-top (CH_3I) molecules at room temperature. In principle, the temperature range over which the current methodology is operating is not limited to room temperature. Higher temperature regimes could be explored, which may help study materials with low vapor pressure. The high degree of orientation in a thermal gas paves the way to unprecedented imaging opportunities, chemical reaction control, and more.

ACKNOWLEDGMENTS

L.X. is a recipient of the Sir Charles Clore Postdoctoral Fellowship. This research was made possible in part by the historic generosity of the Harold Perlman Family.
Appendix A: Impulsive approximation

One of the tools for inducing molecular orientation is a half-cycle THz pulse \[43\]. The interaction of such a pulse with the permanent molecular dipole can be modeled using the potential \( V_{\text{or}}(\theta, t) = -\mu \varepsilon_{\text{or}}(t) \cos(\theta), \) \( (A1) \)

where \( \mu \) is the molecular dipole moment magnitude, \( \varepsilon_{\text{or}}(t) \) defines the electric field’s time dependence, and \( \theta \) is the polar angle between the molecular axis and the electric field vector. For the sake of the model, we assume that \( \varepsilon_{\text{or}}(t) \) is Gaussian

\[
\varepsilon_{\text{or}}(t) = \varepsilon_{0,\text{or}} \exp\left[-t^2/\sigma_{\text{or}}^2\right], \tag{A2}
\]

where \( \varepsilon_{0,\text{or}} \) is the peak amplitude of the electric field, \( \sigma_{\text{or}} \) is the width of the pulse. The equation of motion for the molecular angular momentum \( L \) is

\[
dL/dt = -dV_{\text{or}}(\theta)/dt = -\mu \varepsilon_{\text{or}}(t) \sin(\theta). \tag{A3}
\]

In the impulsive approximation, when the change in \( \theta \) is negligible during the pulse, the change in \( L \) due to the orienting interaction is

\[
\Delta L_{\text{or}} = -\sqrt{2} \pi \mu \sigma_{\text{or}} \varepsilon_{0,\text{or}} \sin(\theta_0). \tag{A4}
\]

where \( \theta_0 \) is the angle at the moment of the pulse, and \( P_{\text{or}} \) is defined as

\[
P_{\text{or}} = \mu \sqrt{I}/\sigma_{\text{or}} \varepsilon_{0,\text{or}}, \tag{A5}
\]

where \( I \) is the molecule’s moment of inertia.

A standard tool for inducing molecular alignment is non-resonant femtosecond laser pulses. We use such a pulse as a prepulse to stratify the phase space, see Sec. II. The interaction of a molecule with the prepulse is modeled as

\[
V_{\text{pre}}(\theta, t) = -\Delta \frac{\Delta \alpha}{4} \frac{\Delta \epsilon_{\text{pre}}(t) \cos^2(\theta)}{\ln(16)}, \tag{A6}
\]

where \( \Delta \alpha \) is the polarizability anisotropy of the molecule. The potential in Eq. (A6) is averaged over the laser’s optical cycle. The function \( \varepsilon_{\text{pre}}(t) \) is the slowly varying Gaussian envelope of the laser pulse

\[
\varepsilon_{\text{pre}}(t) = \varepsilon_{0,\text{pre}} \exp\left[-2 \ln(2) t^2/\sigma_{\text{pre}}^2\right], \tag{A7}
\]

where \( \varepsilon_{0,\text{pre}} \) is the peak amplitude of the laser’s electric field, \( \sigma_{\text{pre}} \) is the full width at half maximum of the laser pulse intensity. In the impulsive approximation

\[
\Delta L_{\text{pre}} = -\sqrt{\frac{\pi}{\ln(16)}} \frac{\Delta \alpha}{4} \sigma_{\text{pre}} \varepsilon_{0,\text{pre}} \sin(2\theta_0), \tag{A8}
\]

and \( P_{\text{pre}} \) is defined as

\[
P_{\text{pre}} = \sqrt{\frac{\pi}{\ln(16)}} \frac{\Delta \alpha}{4T} \sigma_{\text{pre}} \varepsilon_{0,\text{pre}}. \tag{A9}
\]

Appendix B: Orientation factor

Here, we derive the formulas for the orientation factor

\[
\langle \cos(\theta) \rangle (t) = \langle \text{Re}(e^{i\theta}) \rangle (t) = \text{Re} \left[ \langle e^{i\theta} \rangle (t) \right], \tag{B1}
\]

where the angle brackets denote ensemble average, for two cases: (i) excitation by an orienting pulse alone, and (ii) excitation by a prepulse followed by an orienting kick.

1. Single orienting pulse

The time-dependent orientation factor after the orienting excitation is given by the real part of

\[
\langle e^{i\theta} \rangle (t) = (2\pi)^{-3/2} \sigma_T^{-1} \times \int_{-\infty}^{\infty} \int_{0}^{2\pi} \exp\{i[\theta_0 + \omega_0 t - P_{\text{or}} \sin(\theta_0) t]\} \times \exp\{-\omega_0^2/(2\sigma_T^2)\} d\theta_0 d\omega_0 \]

\[
= (2\pi)^{-3/2} \sigma_T^{-1} \int_{-\infty}^{\infty} e^{i\omega_0 t} \exp\{-iP_{\text{or}} \sin(\theta_0) t\} d\omega_0 \]

\[
\times \int_{0}^{2\pi} e^{i\theta_0} \exp\{-iP_{\text{or}} \sin(\theta_0) t\} d\theta_0, \tag{B2}
\]

where \( \sigma_T = \sqrt{k_B T/I} \) and \( \theta(t) = \theta_0 + \omega_0 t - P_{\text{or}} \sin(\theta_0) t \) [see Eq. (1)]. Using the Jacobi–Anger expansion

\[
e^{iz \sin(\theta)} = \sum_{k=\infty}^{\infty} e^{ik\theta} J_k(z), \tag{B3}
\]

where \( J_k(z) \) is the Bessel function of integer order \( k \), we can represent the second integral in Eq. (B2) as

\[
\int_{0}^{2\pi} e^{i\theta_0} \exp\{-iP_{\text{or}} \sin(\theta_0) t\} d\theta_0 \]

\[
= \sum_{k=-\infty}^{\infty} \int_{0}^{2\pi} e^{i\theta_0} e^{-ik\theta_0} J_k(P_{\text{or}} t) d\theta_0 \]

\[
= 2\pi J_1(P_{\text{or}} t), \tag{B4}
\]

where all the terms in the sum, except for \( k = 1 \), vanish.

Finally,

\[
\langle \cos(\theta) \rangle (t) = e^{-\sigma_T^2 t^2/2} J_1(P_{\text{or}} t). \tag{B5}
\]

2. Stratifying prepulse followed by orienting kick

Just after the stratifying kick (prepulse), the rotor’s variables are

\[
\theta_1(t) = \theta_0 + \omega_1 t, \quad \omega_1 = \omega_0 - P_{\text{pre}} \sin(2\theta_0), \tag{B6}
\]

After a delay equal to \( \tau \), at \( t = \tau \), we apply the orienting kick after which the rotor’s variables are

\[
\theta_2(t) = \theta_1(\tau) + (t - \tau) \omega_2, \quad \omega_2 = \omega_1 - P_{\text{or}} \sin[\theta_1(\tau)]. \tag{B7}
\]

The orientation factor is given by the real part of

\[
\langle e^{i\theta} \rangle (t) = \Theta(t - \tau) (2\pi)^{-3/2} \sigma_T^{-1} \int_{-\infty}^{\infty} \int_{0}^{2\pi} \exp\{i\theta_2(t)\} \times \exp\{-\omega_0^2/(2\sigma_T^2)\} d\theta_0 d\omega_0, \tag{B8}
\]

where \( \Theta(t - \tau) \) is the step function. We use Eqs. (B6) and (B7) to express \( \theta_2(t) \) in terms of \( \theta_0 \) and \( \omega_0 \). Next, we use the Jacobi–Anger expansion

\[
\exp\{iP_{\text{or}}(t - \tau) \sin[-\theta_0 - \omega_0 t + P_{\text{pre}} \sin(2\theta_0) t]\}
\]

\[
= \sum_{k=-\infty}^{\infty} \exp\{-ik[\theta_0 + \omega_0 t - P_{\text{pre}} \sin(2\theta_0) t]\} \times J_k[P_{\text{or}}(t - \tau)]] \tag{B9}
\]
Combining the terms proportional to $\omega_0$ in the exponent, we get $\exp[i\omega_0 t - i k \omega_0 \tau]$. Integral $d\omega_0$ then yields
\begin{equation}
\int_{-\infty}^{\infty} \exp[i\omega_0(t - k\tau)]e^{-\omega_0^2/(2\sigma_0^2)} d\omega_0 = \sqrt{2 \pi \sigma_0} e^{-\sigma_0^2(t-k\tau)^2/2}.
\end{equation}

The rest of the terms in the exponent read
\begin{equation}
\exp[i\theta_0 - iP_{pre} \sin(2\theta_0) t - i k \theta_0 + i k P_{pre} \sin(2\theta_0) \tau]
= \exp[i\theta_0(1 - k + iP_{pre} \sin(2\theta_0)(k\tau - t))]
= \sum_{m=-\infty}^{\infty} \exp[i\theta_0(1 - k + 2m)] J_m[P_{pre}(k\tau - t)].
\end{equation}

Integral $d\theta_0$ then yields
\begin{equation}
\int_0^{2\pi} \sum_{m=-\infty}^{\infty} \exp[i\theta_0(1 - k + 2m)] J_m[P_{pre}(k\tau - t)] d\theta_0
= 2\pi \sum_{m=-\infty}^{\infty} \delta(1 - k + 2m) J_m[P_{pre}(k\tau - t)]
= \begin{cases} 2\pi J_{k+1}[P_{pre}(k\tau - t)], & \text{odd } k, \\ 0, & \text{even } k. \end{cases}
\end{equation}

Overall, the orientation signal reads
\begin{equation}
\langle \cos(\theta) \rangle(t) = \Theta(t - \tau) \sum_{\text{odd } k} S_k(t),
\end{equation}
where
\begin{equation}
S_k(t) = e^{-\sigma_0^2(t-k\tau)^2/2} J_{k+1}[P_{pre}(t - \tau)] \times J_{k-1}[P_{pre}(k\tau - t)].
\end{equation}

**Appendix C: Quantum rigid rotor**

The energy eigenstates of the quantum rotor restricted to the XY plane are $\psi_n = \exp(i\eta n)/\sqrt{2\pi}$, where $n = 0, \pm 1, \pm 2, \ldots$. The energies (in atomic units, $h = 1$) are $E_n = n^2/(2I)$, where $I$ is the moment of inertia. Like in the classical case, we treat the effect of the stratifying (prepulse) and orienting kicks in the impulsive approximation. The prepulse transforms an initial wave function $\psi_\prec$ into $\psi_\succ = \exp[iP_{pre} \cos^2(\theta) \tau] \psi_\prec$, where $P_{pre}$ is given by Eq. (A9). Similarly, for the orienting kick $\psi_\prec = \exp[iP_{or} \cos(\theta)] \psi_\prec$, where $F_{or}$ is given by (A5).

Each of the basis wave functions, $\psi_n$ is “kicked” and propagated in time. The final observable, the ensemble averaged orientation factor, $\langle \cos(\theta) \rangle$ is obtained by thermal averaging over the various expectation values $\langle \psi_n(\theta, t) \mid \cos(\theta) \rangle \psi_n(\theta, t) \rangle$, where $\psi_n(\theta, t)$ is the wave function at time $t$ corresponding to the initial state $\psi_n$.

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