

Ionization-induced long-lasting orientation of symmetric-top moleculesLong Xu^{✉,*}, Ilya Tutunnikov^{✉,*}, Yehiam Prior^{✉,†} and Ilya Sh. Averbukh^{✉,‡}*Department of Chemical and Biological Physics, AMOS, The Weizmann Institute of Science, Rehovot 7610001, Israel*

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We theoretically consider the phenomenon of field-free long-lasting orientation of symmetric-top molecules ionized by two-color laser pulses. The anisotropic ionization produces a significant long-lasting orientation of the surviving neutral molecules. The degree of orientation increases with both the pulse intensity and counterintuitively with the rotational temperature. The orientation may be enhanced even further by using multiple-delayed two-color pulses. The long-lasting orientation may be probed by even harmonic generation or by Coulomb-explosion-based methods. The effect may enable the study of relaxation processes in dense molecular gases and may be useful for molecular guiding and trapping by inhomogeneous fields.

DOI: [10.1103/PhysRevA.107.023111](https://doi.org/10.1103/PhysRevA.107.023111)**I. INTRODUCTION**

Field-free-aligned or oriented molecules are essential in many studies, such as ultrafast dynamic imaging, molecular tomography, and electron diffraction, to name just a few. A much more comprehensive list of applications may be found in a recent review by Koch *et al.*, [1]. Naturally, for practical applications, a sizable degree and extended duration of alignment or orientation is beneficial. The effect of laser-induced persistent molecular alignment is well known [2]. Special tailored picosecond laser pulses can be used to align linear molecules in extreme rotational states [3] or to align all the molecular axes of a complex asymmetric-top molecule [4]. Another route to achieving high- and long-lived molecular alignment is by exciting molecules trapped inside helium droplets [5].

The methods for laser-induced molecular *orientation* (especially the long-lasting one) are more challenging and less studied. One of the tools for inducing molecular orientation is a nonresonant two-color laser pulse consisting of the fundamental wave (FW) and its second harmonic (SH). Using such fields, two different orientation mechanisms have been identified and studied theoretically and experimentally [6–12]. The first orientation mechanism, which is dominant at low to moderate (nonionizing) intensities, relies on the interaction of the external fields with the molecular hyperpolarizability, which results in asymmetric torques that orient the molecules along the polarization direction of the SH field [6–8,13,14]. At high (ionizing) intensities, the dominant orientation mechanism [9] is different—probability of ionization depends on the molecular orientation with respect to the polarization direction of the asymmetric electric field of the two-color pulse [9–11]. As a result, immediately after the pulse, the angular distribution of the surviving neutral molecules is asymmetric and has a

nonzero orientation on average. Note that for linear molecules, this orientation disappears shortly after the excitation, but it periodically reemerges due to the phenomenon of rotational quantum revivals [15,16].

Here, we theoretically investigate the ionization-induced orientation of *symmetric-top molecules* excited by intense two-color femtosecond laser pulses. We demonstrate that in addition to the transient postpulse orientation and unlike linear molecules, there also exists a significant long-lasting orientation in these molecules. Long lasting means that the orientation exists not only at the revival times, but also between the revivals. In other words, the orientation signal has a nonzero baseline. Within the idealized model of noninteracting rigid rotors used here, this orientation lasts indefinitely. In practice, however, it will eventually be suppressed by additional physical effects, e.g., by intermolecular collisions in gas cell experiments. Related effects of long-lasting orientation have been recently investigated in chiral [14,17–19] and other nonlinear [14,20,21] molecules excited by nonionizing terahertz (THz) and laser pulses. Persistent orientation may be beneficial in several applications. For example, molecular deflection via scattering off inhomogeneous optical or static fields depends dramatically on the time-averaged molecular orientation (e.g., see Ref. [22]), which may find applications for various separation techniques and methods of chemical analysis. Moreover, in analogy to persistent molecular alignment, persistent orientation may provide access to complementary information on collisional relaxation in dense molecular gases (e.g., see Refs. [23,24]).

In what follows, we present our numerical analysis, outline our results on significant long-lasting orientation, and discuss its dependence on intensity and temperature. We conclude with a discussion of the experimental feasibility of observing the predicted effect.

II. NUMERICAL METHODS

In our analysis, we simulate the rotational dynamics of symmetric-top molecules within the rigid rotor

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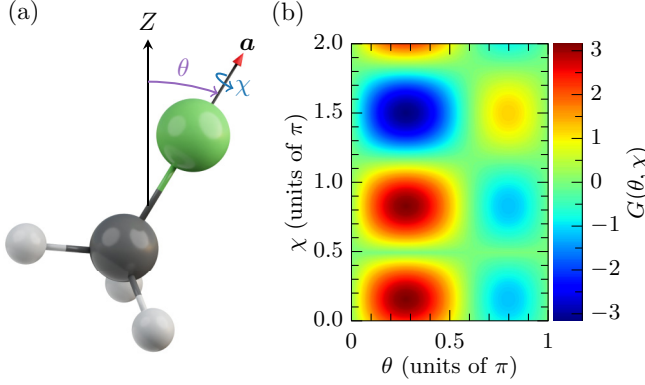


FIG. 1. (a) CH_3F molecule. Atoms are color coded: black, carbon; gray, hydrogen; green, fluorine. θ is the angle between the molecular a axis and the laboratory Z axis, and χ represents the rotation angle about the a axis. (b) Structure factor $G(\theta, \chi)$ [see Eqs. (7) and (8)] determining the angle dependence of the ionization rate.

approximation both classically and quantum mechanically. The symmetric-top molecules are excited by a two-color laser pulse, consisting of the co-linearly polarized and phase-locked FW field and its SH. The electric field is described by

$$\mathbf{E}(t) = E_0 f(t) [\cos(\omega t) + \varepsilon \cos(2\omega t + \phi_0)] \mathbf{e}_Z, \quad (1)$$

where E_0 and ω are the peak amplitude and the carrier frequency of the FW, respectively. The laser pulse envelope is defined by $f(t) = \exp[-2 \ln 2 (t^2/\sigma^2)]$, where σ is the full width at half maximum of the pulse intensity profile, and \mathbf{e}_Z is a unit vector along the laboratory Z axis. Here, we set $\varepsilon = 1$ and $\phi_0 = 0$.

The Hamiltonian describing molecular rotation driven by a two-color laser pulse is given by $H(t) = H_r + H_{\text{int}}$, where H_r is the rotational kinetic-energy Hamiltonian and the interaction Hamiltonian is given by

$$H_{\text{int}} = V_{\text{pol}} + V_{\text{hyp}} + V_{\text{ion}}. \quad (2)$$

The field-polarizability and field-hyperpolarizability interaction terms are defined as [25]

$$V_{\text{pol}} = -\frac{1}{2} \sum_{i,j} \alpha_{ij} E_i E_j, \quad V_{\text{hyp}} = -\frac{1}{6} \sum_{i,j,k} \beta_{ijk} E_i E_j E_k, \quad (3)$$

where E_i , α_{ij} , and β_{ijk} are the components of the electric-field vector, polarizability tensor, and hyperpolarizability tensor, respectively. The ionization depletion term V_{ion} is sensitive to molecular orientation. For linear molecules, e.g., HCl [26] and CO [9,27,28], the ionization rate depends on the angle between the molecular axis and the polarization direction. For symmetric-top molecules, e.g., CH_3F and CH_3Br , belonging to the C_{3v} point group, the ionization rate depends on two angles θ and χ (see Fig. 1) [12].

In this paper, we consider CH_3F as our example symmetric-top molecule. The ionization process is modeled using a complex absorbing potential,

$$V_{\text{ion}} = -\frac{i}{2} \Gamma(\theta, \chi, t), \quad (4)$$

where the ionization rate $\Gamma(\theta, \chi, t)$ is defined as Ref. [12] (within the weak-field asymptotic theory),

$$\Gamma(\theta, \chi, t) = \begin{cases} W(t) |G(\theta, \chi)|^2, & E(t) > 0, \\ W(t) |G(\pi - \theta, \pi + \chi)|^2, & E(t) < 0. \end{cases} \quad (5)$$

Here, $E(t) = \mathbf{e}_Z \cdot \mathbf{E}(t)$, $W(t)$ is the field factor, and $G(\theta, \chi)$ is the structure factor. The field factor is given by [12]

$$W(t) = \frac{\kappa}{2} \left(\frac{4\kappa^2}{|E(t)|} \right)^{2/\kappa-1} \exp \left[-\frac{2\kappa^3}{3|E(t)|} \right], \quad (6)$$

where $\kappa = \sqrt{2I_p}$ and I_p is the field-free energy of the highest occupied molecular orbital (HOMO). We use the following model for the structure factor:

$$G(\theta, \chi) = [\sin(\theta) + \frac{3}{2} \sin(2\theta)] G_1(\chi), \quad (7)$$

where

$$G_1(\chi) = \begin{cases} \sqrt{1 + \sin(3\chi)}, & 0 \leq \chi < 7\pi/6, \\ -\sqrt{1 + \sin(3\chi)}, & 7\pi/6 \leq \chi < 11\pi/6, \\ \sqrt{1 + \sin(3\chi)}, & 11\pi/6 \leq \chi < 2\pi. \end{cases} \quad (8)$$

$G(\theta, \chi)$ defined in Eqs. (7) and (8) closely approximates the structure factor of field-dressed HOMO of CH_3F with the largest dipole moment [12] (the orbital from which the strong field ionization preferentially occurs). The definition in Eq. (5) accounts for the oscillations of the laser electric field along the Z axis. We quantify the degree of orientation of surviving neutral molecules using the thermally averaged quantum expectation value of $\cos(\theta)$, $\langle \cos(\theta) \rangle$. Further details on the quantum simulations can be found in Refs. [21,29] (also see Appendix A).

In classical simulations, we use the Monte Carlo approach to simulate the behavior of a classical ensemble consisting of $N = 10^7$ sample molecules. A detailed description can be found in Refs. [21,30]. Following the ionization depletion, the classical degree of orientation is given by

$$\langle \cos(\theta) \rangle(t) = \sum_{n=1}^N \rho(\theta_n, \chi_n, t) \cos(\theta_n), \quad (9)$$

where the relative weight (nonionized fraction) of the n th molecule is

$$\rho(\theta_n, \chi_n, t) = N_{\text{neu}}^{-1} \exp \left[-\int_0^t \Gamma(\theta_n, \chi_n, t') dt' \right], \quad (10)$$

and the total number of surviving neutral molecules is

$$N_{\text{neu}} = \sum_{n=1}^N \exp \left[-\int_0^t \Gamma(\theta_n, \chi_n, t') dt' \right], \quad (11)$$

Here, θ_n and χ_n are the time-dependent angles of the n th molecule. The population of surviving neutral molecules is defined as N_{neu}/N .

III. RESULTS

Molecular parameters of CH_3F are provided in Appendix B. Figure 2 shows the calculated, classically, and quantum-mechanically, time-dependent orientation factor of neutral molecules following a single two-color pulse applied at $t = 0$. The parameters used in this calculation are as

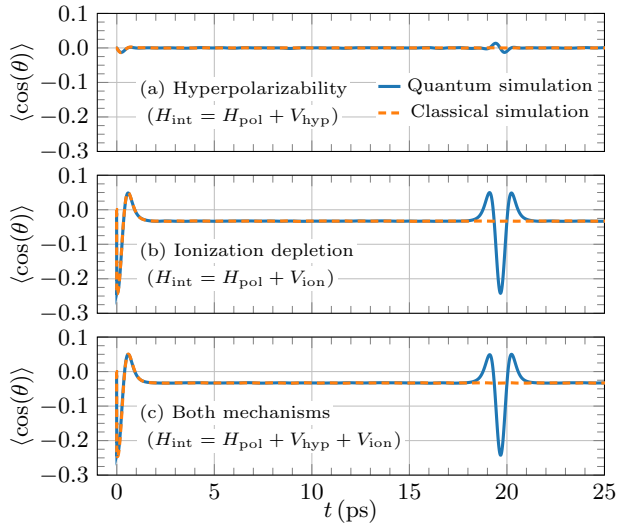


FIG. 2. Time-dependent orientation factor at $T = 300$ K for different orientation mechanisms calculated classically and quantum mechanically. Here the field intensity is $I_0 = 7 \times 10^{13}$ W/cm², and the pulse duration is $\sigma = 20$ fs. About 40% of neutral molecules survive after the ionization.

follows: the rotational temperature is $T = 300$ K, the laser wavelengths are 800 nm (FW) and 400 nm (SH), the peak intensity is 7×10^{13} W/cm², and $\sigma = 20$ fs, see Eq. (1).

The three panels of Fig. 2 show the orientation factor obtained for various combinations of interaction terms [see Eq. (2)]. All cases include the field-polarizability interaction, $V_{\text{pol}} \propto \cos^2(\theta)$ which is a symmetric function of θ (about $\theta = \pi/2$). A torque kick by such a potential results in molecular alignment only (for review, see Ref. [31]). The two other terms V_{hyp} and V_{ion} are asymmetric functions of θ and, thus, induce molecular orientation. All three panels depict the immediate response of $\langle \cos(\theta) \rangle$ to the laser excitation near $t = 0$. This transient orientation effect is similar to the one studied in linear molecules excited by two-color laser pulses [7,8,32–37]. At room temperature and field parameters used here, the transient molecular orientation induced by the field-hyperpolarizability interaction alone [Fig. 2(a)] is negligible compared to the orientation resulting from the ionization depletion [Fig. 2(b)]. Accordingly, the curves in Figs. 2(b) and 2(c) [in which all the interaction terms are included, see Eq. (2)] are almost indistinguishable. These results are consistent with previous results reported for linear molecules [9,11] where it was shown that at high (ionizing) intensities, the orientation mechanism of ionization depletion dominates.

In this paper, we focus on the long-term orientation existing in symmetric-top molecules. Figures 2(b) and 2(c) show that under the stated conditions and for these molecules, following the transient orientation the degree of orientation does not return to zero but persists at a constant value until the first revival and beyond. *This effect of ionization-induced long-lasting orientation does not exist in linear molecules, and it is the main result of this paper.* Note that the quantum and classical results agree well on the short timescale, during the initial transient response, and predict the same degree of long-lasting orientation on the long timescale,

suggesting that the long-lasting orientation stems from a classical origin. Long-lasting orientation has been previously observed in chiral [14,17–19] and studied in other nonlinear molecules [14,20,21] excited by nonionizing THz and laser pulses. In these cases, the orientation mechanisms, including the interactions with the polarizability and hyperpolarizability, were considered. Here, the ionization depletion mechanism gives rise to unprecedented degrees of long-lasting orientation at room temperature. The degree of long-lasting orientation (≈ -0.033) as shown in Figs. 2(b) and 2(c) is an order of magnitude higher than values reported in previous studies.

IV. MECHANISM

Next, we discuss the mechanism behind this large ionization-induced long-lasting orientation. Under the field-free condition, the symmetry axis (dipole) of symmetric-top molecules precesses around the (conserved, space-fixed) vector of angular momentum, whereas, linear molecules rotate in a plane perpendicular to the angular momentum [38]. It is this precession that is the source of the long-lasting orientation in symmetric-top molecules. The degree of long-lasting orientation (with respect to the Z axis) of a single symmetric-top molecule is given by the combination of three quantities $L_a L_Z / L^2$ [20,21], where L_a and L_Z are the projections of the angular momentum along the molecular symmetry axis [the molecular a axis in Fig. 1(a)] and the laboratory Z axis, respectively, and L is the magnitude of the angular momentum. Note that in the presence of Z -polarized pulses, L_a and L_Z are conserved quantities.

Initially, before the laser pulse, the molecules are isotropically distributed in space, namely, there is an equal number of molecules having positive (along the Z axis) and negative (against the Z axis) long-lasting orientations. Therefore, the ensemble-averaged long-lasting orientation $\langle L_a L_Z / L^2 \rangle$ vanishes [21]. The colinearly polarized two-color laser pulse preferentially ionizes molecules oriented more or less along its polarization axis (with $\theta < \pi/2$) [see Fig. 1(b)]. Thus, this selective ionization depletion breaks the symmetry of the molecular ensemble, generating a nonzero long-lasting orientation of the surviving (not ionized) neutral molecules as shown in Figs. 2(b) and 2(c).

For symmetric-top molecules, within the model used here, the long-lasting orientation is permanent. In experiments, however, this orientation will be gradually destroyed by other physical effects such as intermolecular collisions, centrifugal distortion, and radiation emission caused by rapidly rotating molecular permanent dipole moments. Furthermore, whereas the centrifugal distortion is known to lead to the decay of the revivals' peaks due to the dephasing of the rotational states [39,40], the average dipole remains almost unchanged (see Ref. [20]). The radiative emission gradually decreases the rotational energy [39,40], but the relative energy loss during a single revival is negligible for a rarefied molecular gas.

V. INTENSITY DEPENDENCE

One of the ways to enhance the degree of the ionization-induced long-lasting orientation is by increasing the laser pulse energy—peak intensity and/or pulse duration, or invest-

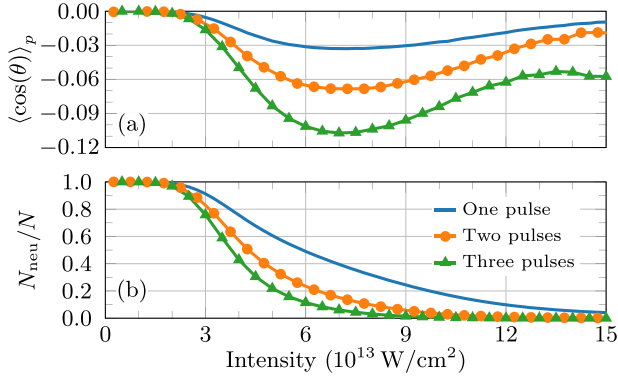


FIG. 3. Classically calculated (a) long-lasting orientation and (b) population of neutral molecules after the pulse(s) as functions of the laser intensity. The time delay between pulses is 0.5 ps. Here $T = 300$ K and $\sigma = 20$ fs. Both orientation mechanisms are taken into account.

ing the higher energy in several pulses. Figure 3 shows the classically calculated long-lasting orientation factor, $\langle \cos(\theta) \rangle_p$ and the population of surviving neutral molecules as functions of the laser intensity for single or multiple delayed pulses. The value of $\langle \cos(\theta) \rangle_p$ is taken after the pulse(s) when the orientation factor reaches a constant value. As expected, with the increasing input energy, the long-lasting orientation factor (in absolute value) initially grows [for $I_0 < 7 \times 10^{13}$ W/cm², see Fig. 3(a)], whereas the population of surviving neutral molecules decreases monotonically [see Fig. 3(b)].

After reaching its maximum value, the long-lasting orientation decreases with increasing laser intensity. The reason for this decrease is the structure factor $G(\theta, \chi)$ shown in Fig. 1(b). Due to the anisotropy of the ionization process, molecules at $\theta \approx 0, 0.6\pi, \pi$ have a relatively low ionization rate. Therefore, when the ionization saturates at high laser intensities, only these molecules survive, but these molecules have a relatively low contribution to the long-lasting orientation. The combination of increased ionization yield, but counterproductive selectivity of low-contributing molecules limits the usefulness of increasing the laser intensity beyond a certain point.

A way to avoid the limits imposed on high intensities is to use multiple pulses instead of a single strong pulse. Consider the application of several delayed two-color pulses. Figure 3(a) shows that the maximum long-lasting orientation is about -0.033 for one pulse, -0.069 for two pulses, and -0.107 for three pulses. Here, the time delay between each pulse is set to 0.5 ps, a relatively long time delay which allows the molecules to rotate between the pulses. This way, after each pulse additional neutral molecules rotate to an orientation more favorable for ionization by the next pulse. This approach overcomes the ionization saturation limit that exists in the case of a single pulse and is similar to the use of multiple pulses for achieving enhanced alignment whereas, avoiding ionization [41,42]. Naturally, adding more pulses results in a progressively lower population of surviving neutral molecules. Nevertheless, for a fixed population, a higher long-lasting orientation is achieved by applying multiple delayed pulses. For example, for $N_{\text{neu}}/N \approx 40\%$, the long-lasting orientation is about -0.033 for one pulse, -0.049 for two

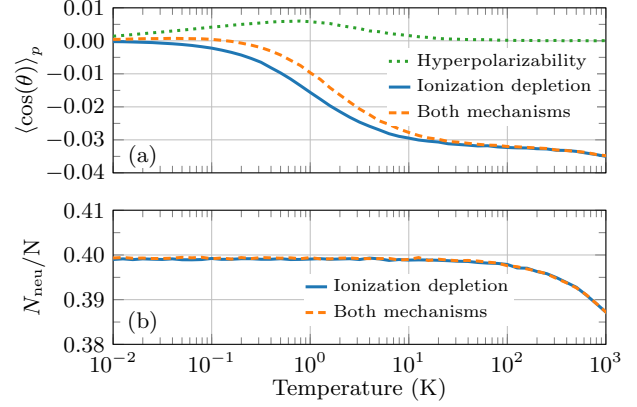


FIG. 4. Classically calculated (a) long-lasting orientation factor and (b) population of neutral molecules as functions of temperature for different orientation mechanisms. The laser parameters are the same as in Fig. 2: $I_0 = 7 \times 10^{13}$ W/cm², $\sigma = 20$ fs. The population for the orientation mechanism of hyperpolarizability remains 1.

pulses, and -0.054 for three pulses. *This observation is an additional main result of this paper.* Optimization of the time delay may allow further enhancement of the long-lasting orientation.

VI. TEMPERATURE DEPENDENCE

Next, we consider the temperature dependence of the long-lasting orientation as depicted in Fig. 4. At $T = 0$, the long-lasting orientation is zero for all three curves shown in Fig. 4(a) as a result of $L_a = L_z = 0$ (these are conserved quantities). There is an optimal temperature ($T < 1$ K in this example) at which the long-lasting orientation induced by the field-hyperpolarizability interaction (together with the field-polarizability interaction) reaches the maximum (≈ 0.006). Above the optimal temperature, the long-lasting orientation decays with increasing temperature [21]. In sharp contrast, the ionization-induced long-lasting orientation factor (in absolute value) increases monotonically with the temperature, which is another principal finding of this paper. As mentioned above, the long-lasting orientation is given by $L_a L_z / L_f^2$, where $L_f = |\mathbf{L}_f|$ is the magnitude of the angular momentum after the pulse. L_z and L_a are conserved in the case of excitation by linearly polarized laser pulses and, thus, are functions of temperature only. The short two-color pulse has a twofold effect: (i) it (almost) instantaneously ionizes the molecules at particular angles (the effect described by V_{ion}), and (ii) it changes the molecular angular momentum $\mathbf{L}_f = \mathbf{L}_i + \delta\mathbf{L}$, where \mathbf{L}_i is the initial angular momentum, and $\delta\mathbf{L}$ is the change caused by V_{pol} . Around the room temperature (in the examples considered here), the effect of V_{pol} becomes negligible, i.e., $L_a L_z / L_f^2 \approx L_a L_z / L_i^2$, and the degree of long-lasting orientation reaches a constant value determined by V_{ion} . At lower temperatures, V_{pol} has a detrimental effect by increasing the total angular momentum such that $L_a L_z / L_f^2 < L_a L_z / L_i^2$ effectively lowers the long-lasting orientation.

At temperatures above room temperature, the ionization can no longer be considered instantaneous because the molecules rotate fast enough to change their orientation dur-

ing the pulse. Accordingly, more molecules get ionized, as seen from the populations in Fig. 4(b). The higher the ionization yield, the higher asymmetry of the molecular ensemble, manifesting in the higher long-lasting orientation.

VII. CONCLUSIONS

We have theoretically demonstrated a sizable ionization-induced long-lasting orientation of symmetric-top molecules excited by two-color laser pulses. The mechanism leading to this observation is the selective ionization of the polar molecules at particular angles with respect to the laser's electric field, and the ability of symmetric-top molecules to precess around the fixed angular momentum vector. We show that using a proper sequence of delayed two-color pulses allows for enhancing the long-lasting orientation of neutral molecules without drastic depletion of their population. Due to the required precession, the enhanced orientation favors high temperature (room temperature and above in our examples). The long-lasting orientation may be measured with the help of Coulomb explosion [11] or by observing second- (or higher-order) harmonic generation in the gas phase, which is sensitive to the lack of inversion symmetry [10,43,44]. Long-lasting orientation can provide complimentary information in studies of relaxation processes in dense molecular gases that are not otherwise accessible (see analogous applications of persistent alignment [23,24]). In addition, molecular focusing, guiding, and trapping by inhomogeneous fields depends on time-averaged molecular orientation [22,45,46]. Thus, the discussed long-lasting orientation mechanism may provide more control in scattering experiments.

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APPENDIX A: QUANTUM SIMULATIONS

In the simulations, the wave-function $|\Psi(t)\rangle$ is expressed in the basis of $|JKM\rangle$ states, where the quantum numbers J , K , and M correspond to the magnitude of the angular momentum, projection of the angular momentum on the molecular symmetry axis, and projection of angular momentum on the laboratory Z axis. We use the random phase wave-functions method (see, e.g., Ref. [47]) to simulate the behavior of the thermal ensemble. We generate L initial states, such as

$$|\psi_l\rangle = \sum_{JKM} \sqrt{\frac{\epsilon_K e^{-E_{JK}/(k_B T)}}{\mathcal{Z}}} |JKM\rangle e^{i\varphi_l, JK M}, \quad (\text{A1})$$

TABLE I. Molecular constants (in atomic units) for CH₃F.

Parameter	Value	Parameter	Value
I_a	20982	$I_b = I_c$	129238
α_{aa}	18.38	$\alpha_{bb} = \alpha_{cc}$	16.76
β_{aaa}	-40.449	$\beta_{abb} = \beta_{acc}$	-26.970
$\beta_{bbb} = -\beta_{bcc}$	11.019	I_p	0.461

where \mathcal{Z} is the partition sum, E_{JK} is the energy/eigenvalue corresponding to the $|JKM\rangle$ state, k_B is the Boltzmann constant, T is the temperature, and $\varphi_{l, JK M} \in [0, 2\pi)$ is a random number. The sum runs over all the thermally populated eigenstates $|JKM\rangle$. For the CH₃F molecule, the statistical weight due to the nuclear spin statistics is given by [48]

$$\epsilon_K = \frac{(2I_{\text{spin}} + 1)^3}{3} \left[1 + \frac{2 \cos(2\pi K/3)}{(2I_{\text{spin}} + 1)^2} \right], \quad (\text{A2})$$

with $I_{\text{spin}} = 1/2$.

Each initial-state $|\psi_l\rangle$ is propagated in time. The time-dependent Schrödinger equation is solved by numerical exponentiation of the Hamiltonian matrix (see EXPOKIT [49]). The time-dependent degree of orientation is given by the average,

$$\langle \cos(\theta) \rangle(t) = \frac{1}{L} \sum_{l=1}^L \langle \cos(\theta) \rangle_l(t), \quad (\text{A3})$$

where $\langle \cos(\theta) \rangle_l(t) \equiv \langle \psi_l(t) | \cos(\theta) | \psi_l(t) \rangle / \langle \psi_l(t) | \psi_l(t) \rangle$ is the orientation factor of surviving neutral molecules, obtained for the l th initial-state $|\psi_l\rangle$.

APPENDIX B: MOLECULAR PARAMETERS

Table I lists the molecular constants of CH₃F. Here, a - c correspond to the principal molecular axes of inertia. Moments of inertia (I_{a-c}) and polarizabilities are taken from NIST [density functional theory, Coulomb-attenuating method with Becke three-parameter Lee-Yang-Parr functional, and augmented correlation-consistent polarized valence triple- ζ Gaussian basis set (CAM-B3LYP/aug-cc-pVTZ)] [50]. Hyperpolarizabilities are from Ref. [51], and the ionization energy I_p is from Ref. [52].

- [1] C. P. Koch, M. Lemeshko, and D. Sugny, Quantum control of molecular rotation, *Rev. Mod. Phys.* **91**, 035005 (2019).
 [2] S. Fleischer, Y. Khodorkovsky, E. Gershnel, Y. Prior, and I. Sh. Averbukh, Molecular alignment induced by ultrashort laser pulses and its impact on molecular motion, *Isr. J. Chem.* **52**, 414 (2012).

- [3] A. A. Milner, A. Korobenko, and V. Milner, Field-free long-lived alignment of molecules with a two-dimensional optical centrifuge, *Phys. Rev. A* **93**, 053408 (2016).
 [4] T. Mullins, E. T. Karamatskos, J. Wiese, J. Onvlee, A. Rouzée, A. Yachmenev, S. Trippel, and J. Küpper, Picosecond pulse-shaping for strong three-dimensional field-free alignment of

- generic asymmetric-top molecules, *Nat. Commun.* **13**, 1431 (2022).
- [5] A. S. Chatterley, C. Schouder, L. Christiansen, B. Shepperson, M. H. Rasmussen, and H. Stapelfeldt, Long-lasting field-free alignment of large molecules inside helium nanodroplets, *Nat. Commun.* **10**, 133 (2019).
- [6] T. Kanai and H. Sakai, Numerical simulations of molecular orientation using strong, nonresonant, two-color laser fields, *J. Chem. Phys.* **115**, 5492 (2001).
- [7] S. De, I. Znakovskaya, D. Ray, F. Anis, N. G. Johnson, I. A. Bocharova, M. Magrakvelidze, B. D. Esry, C. L. Cocke, I. V. Litvinyuk, and M. F. Kling, Field-Free Orientation of CO Molecules by Femtosecond Two-Color Laser Fields, *Phys. Rev. Lett.* **103**, 153002 (2009).
- [8] K. Oda, M. Hita, S. Minemoto, and H. Sakai, All-Optical Molecular Orientation, *Phys. Rev. Lett.* **104**, 213901 (2010).
- [9] M. Spanner, S. Patchkovskii, E. Frumker, and P. Corkum, Mechanisms of Two-Color Laser-Induced Field-Free Molecular Orientation, *Phys. Rev. Lett.* **109**, 113001 (2012).
- [10] E. Frumker, C. T. Hebeisen, N. Kajumba, J. B. Bertrand, H. J. Wörner, M. Spanner, D. M. Villeneuve, A. Naumov, and P. B. Corkum, Oriented Rotational Wave-Packet Dynamics Studies via High Harmonic Generation, *Phys. Rev. Lett.* **109**, 113901 (2012).
- [11] I. Znakovskaya, M. Spanner, S. De, H. Li, D. Ray, P. Corkum, I. V. Litvinyuk, C. L. Cocke, and M. F. Kling, Transition between Mechanisms of Laser-Induced Field-Free Molecular Orientation, *Phys. Rev. Lett.* **112**, 113005 (2014).
- [12] P. M. Kraus, O. I. Tolstikhin, D. Baykusheva, A. Rupenyan, J. Schneider, C. Z. Bisgaard, T. Morishita, F. Jensen, L. B. Madsen, and H. J. Wörner, Observation of laser-induced electronic structure in oriented polyatomic molecules, *Nat. Commun.* **6**, 7039 (2015).
- [13] K. Lin, I. Tutunnikov, J. Qiang, J. Ma, Q. Song, Q. Ji, W. Zhang, H. Li, F. Sun, X. Gong, H. Li, P. Lu, H. Zeng, Y. Prior, I. Sh. Averbukh, and J. Wu, All-optical field-free three-dimensional orientation of asymmetric-top molecules, *Nat. Commun.* **9**, 5134 (2018).
- [14] L. Xu, I. Tutunnikov, Y. Prior, and I. Sh. Averbukh, Three dimensional orientation of small polyatomic molecules excited by two-color femtosecond pulses, *J. Phys. B: At. Mol. Opt. Phys.* **54**, 164003 (2021).
- [15] I. Sh. Averbukh and N. F. Perelman, Fractional revivals: Universality in the long-term evolution of quantum wave packets beyond the correspondence principle dynamics, *Phys. Lett. A* **139**, 449 (1989).
- [16] R. W. Robinett, Quantum wave packet revivals, *Phys. Rep.* **392**, 1 (2004).
- [17] A. A. Milner, J. A. M. Fordyce, I. MacPhail-Bartley, W. Wasserman, V. Milner, I. Tutunnikov, and I. Sh. Averbukh, Controlled Enantioselective Orientation of Chiral Molecules with an Optical Centrifuge, *Phys. Rev. Lett.* **122**, 223201 (2019).
- [18] I. Tutunnikov, J. Floß, E. Gershnel, P. Brumer, I. Sh. Averbukh, A. A. Milner, and V. Milner, Observation of persistent orientation of chiral molecules by a laser field with twisted polarization, *Phys. Rev. A* **101**, 021403(R) (2020).
- [19] I. Tutunnikov, L. Xu, R. W. Field, K. A. Nelson, Y. Prior, and I. Sh. Averbukh, Enantioselective orientation of chiral molecules induced by terahertz pulses with twisted polarization, *Phys. Rev. Res.* **3**, 013249 (2021).
- [20] L. Xu, I. Tutunnikov, E. Gershnel, Y. Prior, and I. Sh. Averbukh, Long-Lasting Molecular Orientation Induced by a Single Terahertz Pulse, *Phys. Rev. Lett.* **125**, 013201 (2020).
- [21] L. Xu, I. Tutunnikov, Y. Prior, and I. Sh. Averbukh, Long-lasting orientation of symmetric-top molecules excited by two-color femtosecond pulses, *Front. Phys.* **9**, 689635 (2021).
- [22] E. Gershnel and I. Sh. Averbukh, Deflection of rotating symmetric top molecules by inhomogeneous fields, *J. Chem. Phys.* **135**, 084307 (2011).
- [23] J.-M. Hartmann and C. Boulet, Quantum and classical approaches for rotational relaxation and nonresonant laser alignment of linear molecules: A comparison for CO₂ gas in the nonadiabatic regime, *J. Chem. Phys.* **136**, 184302 (2012).
- [24] T. Vieillard, F. Chaussard, F. Billard, D. Sugny, O. Faucher, S. Ivanov, J.-M. Hartmann, C. Boulet, and B. Lavorel, Field-free molecular alignment for probing collisional relaxation dynamics, *Phys. Rev. A* **87**, 023409 (2013).
- [25] A. D. Buckingham, Permanent and induced molecular moments and long-range intermolecular forces, in *Advances in Chemical Physics* (Wiley & Sons, New York, 2007), pp. 107–142.
- [26] H. Akagi, T. Otobe, A. Staudte, A. Shiner, F. Turner, R. Dörner, D. M. Villeneuve, and P. B. Corkum, Laser tunnel ionization from multiple orbitals in HCl, *Science* **325**, 1364 (2009).
- [27] H. Li, D. Ray, S. De, I. Znakovskaya, W. Cao, G. Laurent, Z. Wang, M. F. Kling, A. T. Le, and C. L. Cocke, Orientation dependence of the ionization of CO and NO in an intense femtosecond two-color laser field, *Phys. Rev. A* **84**, 043429 (2011).
- [28] J. Wu, L. P. H. Schmidt, M. Kunitski, M. Meckel, S. Voss, H. Sann, H. Kim, T. Jahnke, A. Czasch, and R. Dörner, Multiorbital Tunneling Ionization of the CO Molecule, *Phys. Rev. Lett.* **108**, 183001 (2012).
- [29] I. Tutunnikov, L. Xu, Y. Prior, and I. Sh. Averbukh, Echo-enhanced molecular orientation at high temperatures, *Phys. Rev. A* **106**, L061101 (2022).
- [30] I. Tutunnikov, J. Floß, E. Gershnel, P. Brumer, and I. Sh. Averbukh, Laser-induced persistent orientation of chiral molecules, *Phys. Rev. A* **100**, 043406 (2019).
- [31] H. Stapelfeldt and T. Seideman, Colloquium: Aligning molecules with strong laser pulses, *Rev. Mod. Phys.* **75**, 543 (2003).
- [32] J. Wu and H. Zeng, Field-free molecular orientation control by two ultrashort dual-color laser pulses, *Phys. Rev. A* **81**, 053401 (2010).
- [33] J. H. Mun and H. Sakai, Improving molecular orientation by optimizing relative delay and intensities of two-color laser pulses, *Phys. Rev. A* **98**, 013404 (2018).
- [34] J. H. Mun, H. Sakai, and R. González-Férez, Orientation of linear molecules in two-color laser fields with perpendicularly crossed polarizations, *Phys. Rev. A* **99**, 053424 (2019).
- [35] J. H. Mun and D. E. Kim, Field-free molecular orientation by delay- and polarization-optimized two fs pulses, *Sci. Rep.* **10**, 18875 (2020).
- [36] D. Mellado-Alcedo, N. R. Quintero, and R. González-Férez, Linear polar molecule in a two-color cw laser field: A symmetry analysis, *Phys. Rev. A* **102**, 023110 (2020).
- [37] S. Wang and N. E. Henriksen, Optimal field-free molecular orientation with nonresonant two-color adiabatic-turn-on

- and sudden-turn-off laser pulses, *Phys. Rev. A* **102**, 063120 (2020).
- [38] L. Landau and E. Lifshitz, *Mechanics*, 3rd ed. (Butterworth-Heinemann, Oxford, 1976).
- [39] R. Damari, S. Kallush, and S. Fleischer, Rotational Control of Asymmetric Molecules: Dipole- versus Polarizability-Driven Rotational Dynamics, *Phys. Rev. Lett.* **117**, 103001 (2016).
- [40] P. Babilotte, K. Hamraoui, F. Billard, E. Hertz, B. Lavorel, O. Faucher, and D. Sugny, Observation of the field-free orientation of a symmetric-top molecule by terahertz laser pulses at high temperature, *Phys. Rev. A* **94**, 043403 (2016).
- [41] M. Leibscher, I. Sh. Averbukh, and H. Rabitz, Molecular Alignment by Trains of Short Laser Pulses, *Phys. Rev. Lett.* **90**, 213001 (2003).
- [42] M. Leibscher, I. Sh. Averbukh, and H. Rabitz, Enhanced molecular alignment by short laser pulses, *Phys. Rev. A* **69**, 013402 (2004).
- [43] E. Frumker, N. Kajumba, J. B. Bertrand, H. J. Wörner, C. T. Hebeisen, P. Hockett, M. Spanner, S. Patchkovskii, G. G. Paulus, D. M. Villeneuve, A. Naumov, and P. B. Corkum, Probing Polar Molecules with High Harmonic Spectroscopy, *Phys. Rev. Lett.* **109**, 233904 (2012).
- [44] P. M. Kraus, A. Rupenyan, and H. J. Wörner, High-Harmonic Spectroscopy of Oriented OCS Molecules: Emission of Even and Odd Harmonics, *Phys. Rev. Lett.* **109**, 233903 (2012).
- [45] E. Gershnel and I. Sh. Averbukh, Electric deflection of rotating molecules, *J. Chem. Phys.* **134**, 054304 (2011).
- [46] J. Küpper, F. Filsinger, G. Meijer, and H. Stapelfeldt, Manipulating the motion of complex molecules: Deflection, focusing, and deceleration of molecular beams for quantum-state and conformer selection, in *Methods in Physical Chemistry* (Wiley, Hoboken, NJ, 2012), Chap. 1, pp. 1–28.
- [47] S. Kallush and S. Fleischer, Orientation dynamics of asymmetric rotors using random phase wave functions, *Phys. Rev. A* **91**, 063420 (2015).
- [48] R. S. McDowell, Rotational partition functions for symmetric-top molecules, *J. Chem. Phys.* **93**, 2801 (1990).
- [49] R. B. Sidje, Expokit: A software package for computing matrix exponentials, *ACM Trans. Math. Softw.* **24**, 130 (1998).
- [50] R. D. Johnson, NIST Computational chemistry comparison and benchmark database, Release 20, Technical Report, (2019) <http://cccbdb.nist.gov>.
- [51] D. P. Chong, Theoretical calculations of dipole moments, polarizabilities, and hyperpolarizabilities of HF, OCS, O₃, CH₃F, and CH₃Cl by local density approximation, *J. Chin. Chem. Soc.* **39**, 375 (1992).
- [52] G. Bieri, L. Åsbrink, and W. Von Niessen, 30.4-nm He(II) photoelectron spectra of organic molecules: Part IV. fluorocompounds (C, H, F), *J. Electron Spectrosc. Relat. Phenom.* **23**, 281 (1981).