

# Rotational dephasing of the molecular alignment by centrifugal distortion [Invited]

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The dephasing of molecular alignment can lead to the deformation of the alignment signal during its periodic revivals. Most studies are concentrated on the first few rotational revival periods of the molecular alignment and neglect the dephasing effect. However, study of the alignment dephasing is still of great significance for both the long-term dynamics of the molecular alignment and the dephasing itself. In this work, we theoretically demonstrate that the dephasing effect is correlated with both the rotational temperature and the rotational revival period of the molecules. The results present that the dephasing is especially significant for those molecules with long rotational revival period at high rotational temperatures. The physics behind it is explored by taking advantage of the coherence of the rotational quantum state population. This work deepens our understanding of rotational dynamics and rotational spectroscopy in molecular alignment.

**Keywords:** dephasing; molecular alignment; centrifugal distortion; rotational state population.

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## 1. Introduction

Over the past few decades, molecular alignment has been extensively studied due to its wide application in various related fields, such as chemical reaction dynamics<sup>[1,2]</sup>, high-order harmonic generation<sup>[3,4]</sup>, attosecond science<sup>[5,6]</sup>, and echoes<sup>[7-9]</sup>. Generally, the alignment is called to be created when the order of the molecular geometry, i.e., the molecular axis by considering the linear molecule for most cases, is defined with respect to a space fixed axis. A strong, linearly polarized picosecond or femtosecond laser pulse has proven to be the most versatile technique to align molecules<sup>[10,11]</sup>. Two alternative ways of molecular alignment can be generated depending on the comparison between the pulse duration of the laser pulse and the rotational period of the molecule. One case is that the pulse duration of the laser pulse is far longer than the rotational period of the molecule<sup>[12]</sup>. The laser pulse can be regarded as turning on and off slowly during interaction with the molecular ensemble. The molecule smoothly aligns as the laser pulse turns on and returns to the isotropic angular distribution along with the laser pulse fading away. The alignment proceeds adiabatically and is termed as the “adiabatic alignment.” The other case is the impulsive alignment or the so called “nonadiabatic alignment”<sup>[13-15]</sup>. In this case, the laser pulse duration is much shorter than the rotational period of the molecule. Field-free periodic rotational revivals can be formed after the impulsive interaction. This field-free scenario provides great convenience for various related studies, for instance, dynamics of the molecular alignment<sup>[16]</sup>.

In the nonadiabatic alignment, the interaction between the impulsive laser field and the molecule can be treated as a “kick.” The kick leads to the molecule in a coherent superposition of rotational eigenstates, i.e., to form a wavepacket<sup>[17-19]</sup>. The wavepacket experiences periodic dephasing and rephasing of its rotational components during the free evolution and thus the molecular alignment periodically reproduced at multiple revivals<sup>[20]</sup>. Under an ideal circumstance when the linear molecule is considered as a strictly rigid rotor, the periodically reconstructed alignment can maintain for a long time until the coherence is broken by the collision with other molecules. However, real molecules have finite rigidity and are sensitive to the centrifugal force caused by their fast spinning, preventing the perfect recurrence of the molecular alignment<sup>[21]</sup>. This deformation of the alignment signals is called “dephasing” of the molecular alignment. In this work, we theoretically demonstrate the rotational dephasing effect of the molecular alignment caused by considering the centrifugal distortion. The deformation caused by dephasing manifests in the lowering of the alignment signals and the increasing number of oscillations during its rotational revivals. We show that the dephasing can be affected by both the rotational temperature and the rotational revival period of the molecules. The dephasing effect is more significant with higher rotational temperature and longer rotational period. Finally, the physics behind the dephasing is presented by considering the rotational quantum state population at different temperatures for various molecules.

## 2. Theoretical Method

The theory of the laser-induced nonresonant molecular alignment has been thoroughly introduced in numerous previous works and is briefly presented here. Suppose a molecular ensemble is exposed to a nonresonant linearly polarized femtosecond laser field,

$$E(t) = E_0 f(t) \cos \omega t, \quad (1)$$

with the Gaussian distribution

$$f(t) = \exp[-(2 \ln 2)t^2/\tau^2], \quad (2)$$

where  $\omega$  is the laser carrier frequency, and  $\tau$  is the pulse duration. As a result, a torque is exerted to the molecules due to the interaction-induced anisotropic polarizability  $\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp}$  with  $\alpha_{\parallel}$  and  $\alpha_{\perp}$ , respectively, the polarizability components parallel and perpendicular to the molecular axis. The molecules thus rotate toward the laser polarized direction to generate transient molecular alignment. The Hamiltonian describing the rotational dynamics can be written by

$$H(t) = E_J - V(t) = hcBJ(J + 1) - (1/2)E^2(t)(\Delta\alpha \cos^2 \theta + \alpha_{\perp}), \quad (3)$$

where the first term  $E_J$  and the second term  $V(t)$ , respectively, represent the rotational energy and the laser field–molecule interaction energy,  $h$  is Planck's constant,  $c$  is the light velocity in vacuum,  $B$  is the rotational constant of the molecule,  $J$  is the quantum number of the rotational angular momentum, and  $\theta$  is the angle between the molecular axis and the polarization direction of the laser field. The quantization of the rotational angular momentum indicates the excitation dynamics periodic revivals, which results in the molecular alignment manifesting perfect periodic recurrences with the rotational revival period  $T_{\text{rev}} = 1/(2Bc)$ . However, real molecules are not ideal rigid rotors. Another term called “centrifugal distortion” should be considered because of fast spinning of the molecule, especially for those with increasing angular momentum ( $J$ ). Thus, the rotational energy in Eq. (3) is rewritten as  $E_J = hcBJ(J + 1) - hcDJ^2(J + 1)^2$ , where  $D$  is the centrifugal distortion constant, and the typical value of ratio  $D/B$  is in a range of  $10^{-5}$ – $10^{-7}$ .

The molecular alignment is usually characterized by the expectation value of  $\cos^2 \theta$  (i.e.,  $\langle \cos^2 \theta \rangle$ ) with

$$\langle \cos^2 \theta \rangle = \langle \psi_{JM} | \cos^2 \theta | \psi_{JM} \rangle, \quad (4)$$

where  $\psi_{JM}$  is the rotational wavepacket formed by the interaction with the laser field. Notice that the expectation value should be averaged over the Boltzmann distribution of the initial rotational state because of the thermal equilibrium of the molecular ensemble. In addition, the spin statistics of the nuclei ought to be considered that results in the populations of odd and even rotational components for different proportions<sup>[22]</sup>. Molecular parameters used in our calculations are listed in Table 1.

Table 1. Molecular Parameters Used in the Calculations.

Molecule	$B$ [ $\text{cm}^{-1}$ ]	$D$ [ $\text{cm}^{-1}$ ]	$D/B$ [ $\times 10^{-7}$ ]	$\Delta\alpha$ [ $\text{\AA}^3$ ]	$T_{\text{rev}}$ [ps]
CO	1.93 <sup>a</sup>	$6.1 \times 10^{-6a}$	31.6	0.524 <sup>b</sup>	8.64
CO <sub>2</sub>	0.3902 <sup>c</sup>	$1.19 \times 10^{-7c}$	3.05	2.0 <sup>d</sup>	42.7
OCS	0.2039 <sup>a</sup>	$0.43 \times 10^{-7a}$	2.11	4.67 <sup>a</sup>	81.7

<sup>a</sup>From NIST, <https://physics.nist.gov/PhysRefData/MolSpec>.

<sup>b</sup>From Ref. [13].

<sup>c</sup>From Ref. [23].

<sup>d</sup>From Ref. [7].

Laser parameters are set as follows: the carrier frequency is  $\omega = 12,500 \text{ cm}^{-1}$ , the pulse duration is  $\tau = 100 \text{ fs}$ , and the peak intensity is  $I = 1 \times 10^{13} \text{ W/cm}^2$ .

## 3. Results and Discussion

Taking CO molecules as a sample, we first present the time-evolved molecular alignment with three different rotational temperatures, i.e., the ambient temperature  $T = 300 \text{ K}$ , the medium case  $T = 100 \text{ K}$ , and a relatively low event  $T = 30 \text{ K}$ , and the results are shown in Fig. 1. In order to completely observe the dephasing process, more than 20 rotational periods of the revivals ( $T_{\text{rev}} = 8.64 \text{ ps}$  for CO molecules) are demonstrated. One can see from Fig. 1(a) that, along with the alignment evolving, the amplitude of the alignment signal (quantified by peak-to-peak difference) gradually decreases, accompanied by an increasing number of oscillations<sup>[24]</sup>. After more than 20 rotational revival periods have elapsed, the dephasing is significantly obvious. As compared to that of the case  $T = 300 \text{ K}$ , Fig. 1(b) shows that the

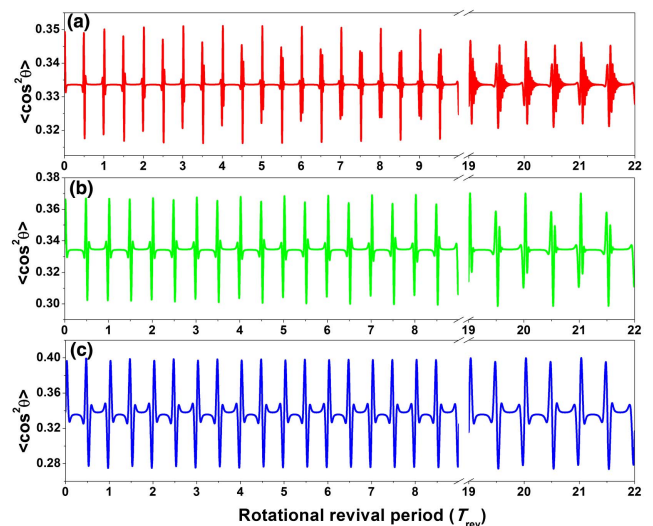


Fig. 1. Time-evolved molecular alignment of CO molecules at the rotational temperature (a)  $T = 300 \text{ K}$ , (b)  $100 \text{ K}$ , and (c)  $30 \text{ K}$ .

dephasing is not evident for the initial few revivals of the medium state  $T = 100$  K. Even after 20 periods of the revival, the deformation caused by the dephasing does not destroy the general structure of the alignment but only with a somewhat decrease of the signal amplitude. At a very low rotational temperature  $T = 30$  K, however, nearly no dephasing can be observed for all the considered revival periods, as is shown in Fig. 1(c). These results demonstrate that the dephasing effect should be paid attention to at high ambient temperatures, while it can be almost negligible for low rotational temperatures. In order to observe the effect of the temperature on the dephasing in further detail, we present in Fig. 2(a) the amplitude of the alignment signals as a function of the rotational revival period at various rotational temperatures. Like the results shown in Fig. 1, the dephasing effect (manifesting in increased difference of the signal amplitude) gradually enlarges along with the increase of the temperature, while almost disappearing at lower cases. Detailed analysis demonstrates that the critical temperature for the emergence of the dephasing is  $\sim T = 70$  K, as is displayed in Fig. 2(b). Under this temperature, the decrease of the signal amplitude induced by dephasing is almost disappears in all revival periods.

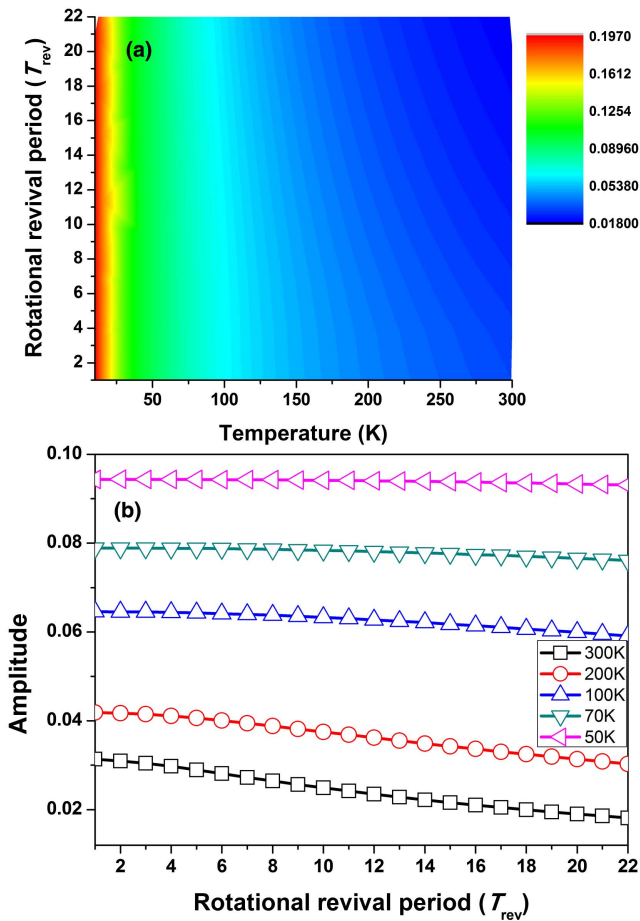


Fig. 2. (a) Contour plots in 2D for the amplitude of the alignment signals at different rotational temperatures. (b) Line plots of several typical temperatures in (a).

Next, we further explore the relationship between the dephasing effect and the molecular rotational periods of different molecules. Figure 3 presents the alignment dynamics of the 10th revival for CO, CO<sub>2</sub>, and OCS molecules at the same rotational temperature  $T = 300$  K. One can see the dephasing significantly emerges for the OCS molecule while just appears for CO and CO<sub>2</sub> molecules. Notice that the  $D/B$  value of the CO<sub>2</sub> molecule is an order of magnitude smaller than that of the CO molecule (see Table 1). Thus, one can infer that the CO<sub>2</sub> molecule also suffers from severe dephasing if it was assumed its  $D/B$  value is as large as the CO molecule. Considering the difference in their respective rotational revival periods ( $T_{rev} = 8.64$  ps for CO and  $T_{rev} = 42.7$  ps for CO<sub>2</sub> molecules), one can reasonably draw that, under the condition that the  $D/B$  values are not too different, the longer the rotational revival period is, the easier the molecular alignment is to dephasing. This can be verified by further comparing the cases of CO<sub>2</sub> to OCS molecules shown in Figs. 3(b) and 3(c). The  $D/B$  values for the two molecules differ by less than double, and the value of the OCS molecule is even smaller than that of the CO molecule. However, the dephasing is more rapid for the OCS molecule due to its longer revival period.

In what follows, we present a theoretical explanation of the alignment dephasing discussed above by considering the populations in different rotational quantum states. The rotational

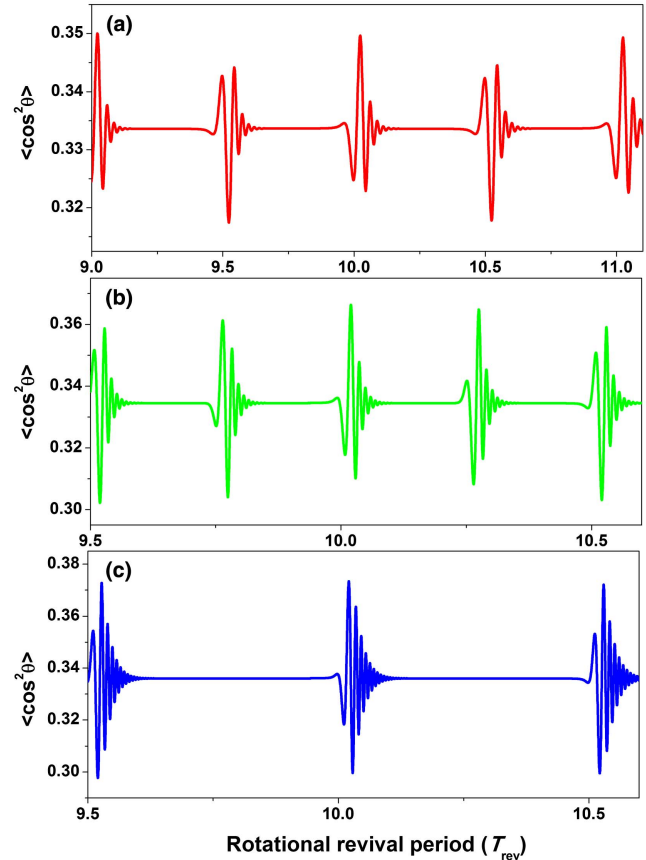


Fig. 3. Time-evolved molecular alignment around the 10th  $T_{rev}$  of (a) CO, (b) CO<sub>2</sub>, and (c) OCS molecules at the rotational temperature  $T = 300$  K.

wavepacket created by field–molecule interaction can be expressed as

$$\psi_{JM}(t) = \sum_{J,M} A_{J,M}(t) |J, M\rangle, \quad (5)$$

where  $A_{J,M}(t)$  is the expansion coefficients of the eigenstates  $|J, M\rangle$ . It is noted that the magnetic quantum number  $M$  is conserved in the linearly polarized laser field and omitted in the following discussions for convenience. Once created, the time-evolved rotational wavepacket under field-free Hamiltonian can be written as

$$\psi_J(t) = \sum_J A_J(t) e^{-i\hat{H}t/\hbar} |J\rangle = \sum_J A_J(t) e^{-iE_J t/\hbar} |J\rangle, \quad (6)$$

where  $E_J = hcBJ(J+1) - hcDJ^2(J+1)^2$ . Taking into account Eq. (6), the expectation value of the alignment can be calculated with the selection rule  $J \rightarrow J' = J, J \pm 2$ . It is simple that molecular alignment from the transitions  $J \rightarrow J' = J$  is independent of the time evolution. Thus, the time-dependent alignment signals governed by  $J \rightarrow J' = J \pm 2$  is of interest and given by<sup>[20]</sup>

$$\begin{aligned} S(t) &\propto \langle \psi_J(t) | \cos^2\theta | \psi_J(t) \rangle \\ &\propto \sum_J C_J(t) \exp[-i(E_{J+2} - E_J)t/\hbar] + \text{c.c.}, \end{aligned} \quad (7)$$

with  $C_J(t) \equiv A_J^*(t)A_{J+2}(t)\langle J | \cos^2\theta | J+2 \rangle$  and  $E_{J+2} - E_J = 2hcB(2J+3) - 4hcD(2J^3 + 9J^2 + 15J + 9)$ . Substituting the expression of  $(E_{J+2} - E_J)$  to Eq. (7), one can obtain

$$\begin{aligned} S(t) &\propto \sum_J C_J(t) \exp[-i4\pi Bc(2J+3)t] \\ &\cdot \exp[i8\pi Dc(2J^3 + 9J^2 + 15J + 9)t] + \text{c.c.} \end{aligned} \quad (8)$$

for the molecular alignment at the time of full rotational revival period  $t = nT_{\text{rev}} = n/(2Bc)$  ( $n$  is an integer), and the value of the first exponential term in Eq. (8) is one. Thus, the alignment signal at the full time revival is governed by the second exponential term and takes the form

$$\begin{aligned} S(nT_{\text{rev}}) &\propto \sum_J C_J(t) \exp[i4\pi n(D/B) \\ &\cdot (2J^3 + 9J^2 + 15J + 9)] + \text{c.c.} \end{aligned} \quad (9)$$

Equation (9) demonstrates that a phase in terms of the rotational quantum numbers  $J$  is accumulated in each revival period of the molecular alignment, which includes a global phase [Eq. (9)], a linear phase ( $15J$ ), a quadratic dispersion ( $9J^2$ ), and a third-order dispersion ( $2J^3$ ). It is pointed out that the cubic term dominates the multiple oscillations displayed in the alignment dephasing<sup>[25,26]</sup>. As shown in Figs. 4(a)–4(c), the most populated rotational states of the CO molecule at  $T = 30$  K, 100 K, and 300 K are  $J = 2, 4,$  and  $7,$  respectively. According to Eq. (9), only the case  $J = 7$  results in the third-order

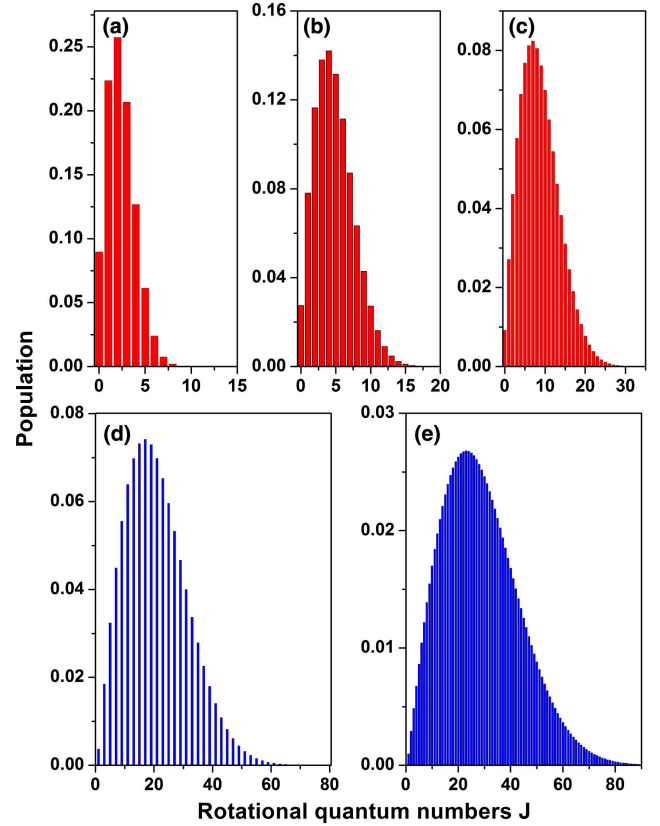


Fig. 4. Rotational state population of (a)–(c) CO, (d) CO<sub>2</sub>, and (e) OCS molecules at the rotational temperature (a)  $T = 30$  K, (b) 100 K, and (c)–(e) 300 K.

dispersion being dominant and leads to obvious dephasing after a few rotational revivals, as Fig. 1(a) presents. To CO<sub>2</sub> and OCS molecules, however, one can see from Figs. 4(d) and 4(e) that the most populated states at  $T = 300$  K are, respectively,  $J = 17$  and  $23$  because of their smaller rotational constants, i.e., longer rotational revival periods. Although the  $D/B$  value of the OCS molecule is relatively smaller than that of the CO<sub>2</sub> ( $2.11 \times 10^{-7}$  versus  $3.05 \times 10^{-7}$ , see Table 1), it remains that the dephasing effect of the OCS molecule is greater due to its larger most populated state, as can be inferred from Eq. (9) and the molecular alignment demonstrated in Fig. 3.

#### 4. Conclusion

To conclude, we show in this work the dephasing effect of the molecular alignment induced by centrifugal distortion. The calculation results demonstrate that the dephasing is especially significant for those molecules with long rotational revival period at high rotational temperatures. In addition to reducing the degree of molecular alignment, the dephasing can also cause multiple oscillations of the alignment signal after several revival periods. Only at relatively low rotational temperatures can the molecular alignment be perfectly reconstructed for a great number of revivals. The physics behind these conclusions can be perfectly explained by the coherent populations of the molecular

rotational states. The study provides a perspective to gain insight into the coherence of the molecular rotational states and further the dynamics of the rotational wavepacket.

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## References

1. Y.-P. Chang, K. Długołęcki, J. Küpper, D. Rösch, D. Wild, and S. Willitsch, "Specific chemical reactivities of spatially separated 3-aminophenol conformers with cold  $\text{Ca}^+$  ions," *Science* **342**, 98 (2013).
2. I. V. Litvinyuk, K. F. Lee, P. W. Dooley, D. M. Rayner, D. M. Villeneuve, and P. B. Corkum, "Alignment-dependent strong field ionization of molecules," *Phys. Rev. Lett.* **90**, 233003 (2003).
3. T. Kanai, S. Minemoto, and H. Sakai, "Ellipticity dependence of high-order harmonic generation from aligned molecules," *Phys. Rev. Lett.* **98**, 053002 (2007).
4. M. Li, G. Jia, and X. Bian, "Alignment dependent ultrafast electron-nuclear dynamics in molecular high-order harmonic generation," *J. Chem. Phys.* **146**, 084305 (2017).
5. P. Lan, P. Lu, W. Cao, Y. Li, and X. Wang, "Carrier-envelope phase-stabilized attosecond pulses from asymmetric molecules," *Phys. Rev. A* **76**, 021801 (2007).
6. C. Jin, S. Wang, X. Zhao, S. Zhao, and C. Lin, "Shaping attosecond pulses by controlling the minima in high-order harmonic generation through alignment of  $\text{CO}_2$  molecules," *Phys. Rev. A* **101**, 013429 (2020).
7. G. Karras, E. Hertz, F. Billard, B. Lavorel, J.-M. Hartmann, O. Faucher, E. Gershnabel, Y. Prior, and I. S. Averbukh, "Orientation and alignment echoes," *Phys. Rev. Lett.* **114**, 153601 (2015).
8. L. Xu, I. Tutunnikov, L. Zhou, K. Lin, J. Qiang, P. Lu, Y. Prior, I. S. Averbukh, and J. Wu, "Echoes in unidirectionally rotating molecules," *Phys. Rev. A* **102**, 043116 (2020).
9. S. Xu, G. Liu, and Y. Huang, "Creating alignment echoes using a phase-shaped femtosecond laser pulse," *J. Phys. B* **55**, 155401 (2022).
10. H. Stapelfeldt and T. Seideman, "Colloquium: aligning molecules with strong laser pulses," *Rev. Mod. Phys.* **75**, 543 (2003).
11. T. Seideman and E. Hamilton, "Nonadiabatic alignment by intense pulses. concepts, theory, and directions," *Adv. At. Mol. Opt. Phys.* **52**, 289 (2006).
12. R. Torres, R. Nalda, and J. P. Marangos, "Dynamics of laser-induced molecular alignment in the impulsive and adiabatic regimes: a direct comparison," *Phys. Rev. A* **72**, 023420 (2005).
13. S. Zhang, C. Lu, T. Jia, Z. Sun, and J. Qiu, "Field-free molecular alignment control by phase-shaped femtosecond laser pulse," *J. Chem. Phys.* **135**, 224308 (2011).
14. S. Xu, Y. Yao, C. Lu, J. Ding, T. Jia, S. Zhang, and Z. Sun, "Manipulating field-free molecular alignment by V-shaped femtosecond laser pulses," *Phys. Rev. A* **89**, 053420 (2014).
15. S. Fleischer, Y. Khodorkovsky, E. Gershnabel, Y. Prior, and I. S. Averbukh, "Molecular alignment induced by ultrashort laser pulses and its impact on molecular motion," *Isr. J. Chem.* **52**, 414 (2012).
16. J. Liu, Q. Cheng, D. Yue, X. Zhou, and Q. Meng, "Dynamical analysis of the effect of elliptically polarized laser pulses on molecular alignment and orientation," *Chin. Opt. Lett.* **16**, 103201 (2018).
17. Y. Gao, C. Wu, N. Xu, G. Zeng, H. Jiang, H. Yang, and Q. Gong, "Manipulating molecular rotational wave packets with strong femtosecond laser pulses," *Phys. Rev. A* **77**, 043404 (2008).
18. Y. Huang and S. Xu, "Controlling population of the molecular rotational state and the alignment theoretically by tailored femtosecond laser pulse," *R. Soc. Open Sci.* **5**, 171502 (2018).
19. Y. Huang and S. Xu, "Evolution of the rotational quantum state in field-free molecular alignment and orientation," *Eur. Phys. J. D* **75**, 181 (2021).
20. P. W. Dooley, I. V. Litvinyuk, K. F. Lee, D. M. Rayner, M. Spanner, D. M. Villeneuve, and P. B. Corkum, "Direct imaging of rotational wavepacket dynamics of diatomic molecules," *Phys. Rev. A* **68**, 023406 (2003).
21. D. Rosenberg, R. Damari, S. Kallush, and S. Fleischer, "Rotational echoes: rephasing of centrifugal distortion in laser-induced molecular alignment," *J. Phys. Chem. Lett.* **8**, 5128 (2017).
22. S. Zhang, C. Lu, T. Jia, Z. Wang, and Z. Sun, "Controlling field-free molecular orientation with combined single- and dual-color laser pulses," *Phys. Rev. A* **83**, 043410 (2011).
23. H. Pan, X.-F. Li, Y. Lu, A.-W. Liu, V. I. Perevalov, S. A. Tashkun, and S.-M. Hu, "Cavity ring down spectroscopy of  $^{18}\text{O}$  and  $^{17}\text{O}$  enriched carbon dioxide near 795 nm," *J. Quant. Spectrosc. Radiat. Transfer* **114**, 42 (2013).
24. G. Brügger, H. M. Frey, P. Steinegger, P. Kowalewski, and S. Leutwyler, "Femtosecond rotational Raman coherence spectroscopy of cyclohexane in a pulsed supersonic jet," *J. Phys. Chem. A* **115**, 12380 (2011).
25. U. Lev, L. Graham, C. B. Madsen, I. Ben-Itzhak, B. D. Bruner, B. D. Esry, H. Frostig, O. Heber, A. Natan, V. S. Prabhudesai, D. Schwalm, Y. Silberberg, D. Strasser, I. D. Williams, and D. Zajfman, "Quantum control of photodissociation using intense, femtosecond pulses shaped with third order dispersion," *J. Phys. B* **48**, 201001 (2015).
26. Y. Huang, S. Xu, Y. Yao, T. Jia, S. Zhang, and Z. Sun, "Enhancing field-free molecular alignment by a polynomial phase modulation," *Eur. Phys. J. D* **70**, 9 (2016).