Molecular spinning by a chiral train of short laser pulses

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We provide a detailed theoretical analysis of molecular rotational excitation by a chiral pulse train, a sequence of linearly polarized pulses with the polarization direction rotating from pulse to pulse by a controllable angle. Molecular rotation with a preferential rotational sense (clockwise or counterclockwise) can be excited by this scheme. We show that the directionality of the rotation is caused by quantum interference of different excitation pathways. The chiral pulse train is capable of selective excitation of molecular isotopologs and nuclear spin isomers in a mixture. We demonstrate this using ${}^{14}N_2$ and ${}^{15}N_2$ as examples for isotopologs and para- and ortho-nitrogen as examples for nuclear-spin isomers.

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I. INTRODUCTION

The control of rotational molecular dynamics by nonresonant strong laser fields has proven to be a powerful tool. It allows creating ensembles of aligned [1–5], oriented [6,7], or planarly confined molecules [8–13]. The proposed and realized applications are numerous, including control of chemical reactions [2,14], high-order-harmonic generation [15,16], control of molecular collisions with atoms [17] or surfaces [18–22], and deflection [23–25] of molecules by external fields.

An important challenge for strong-field rotational control is selective excitation in a mixture of different molecular species. Isotopolog selective control was demonstrated in Refs. [26–28] using constructive and destructive interference induced by a pair of delayed laser pulses [29]. With a similar scheme also nuclear-spin isomer selective excitation was achieved [27,30,31]. More recently, isotopolog selective rotational excitation by periodic pulse trains has been demonstrated [32], and the connection of this scheme to the problem of Anderson localization was shown [33].

One current direction of strong-field rotational control focuses on the excitation of molecular rotation with a preferred sense of the rotation. In the "optical centrifuge" approach [8,34–36], the molecules are subject to two counterrotating circularly polarized fields, which are linearly chirped with respect to each other. The resulting interaction potential creates an accelerated rotating trap, bringing the molecules to a fast-spinning state. The alternative "double-pulse" scheme reaches the same goal by using two properly timed linearly polarized pulses [9,10]. The first pulse induces molecular alignment. When the alignment reaches its peak, the second pulse, whose polarization is rotated by 45° with respect to the first one, is applied and induces the directed rotation. More recently, an approach using a "chiral pulse train" was demonstrated [37], in which a train of pulses is used, where the pulse polarization is changed by a constant angle from pulse to pulse (see Fig. 1).

In this article, we provide a detailed theoretical analysis of the rotational excitation by a chiral pulse train demonstrated in Ref. [37]. A thorough description of the experimental procedure is presented in a companion article [38].

For the present article, the structure is as follows. In Sec. II we introduce the model for the laser-molecule interaction.

Then, we consider excitation scenarios for two kinds of molecules. The first one is N_2 , representing a simple diatomic molecule which is well described by the standard model of a rigid rotor. The second molecule we consider is O_2 . Unlike the nitrogen molecule, it has a nonzero electronic spin in its ground state, leading to a more complex structure of the rotational levels. Our analytical and numerical results are presented in Sec. III. Here, we first show the results for the excitation of $^{14}N_2$ by a chiral train of equally strong pulses. Next, we demonstrate the prospects of selective excitation of nuclear-spin isomers and isotopologs by such trains. Finally, the results for oxygen molecules interacting with a train of unequal pulses are shown and compared with the experiment [37]. In the last section, we summarize the results and conclude.

II. MODEL AND NUMERICAL TREATMENT

A. Model

We consider the following scenario: A train of ultrashort laser pulses interacts with a gas sample of linear molecules such as N₂ or O₂. The pulses are applied with a constant delay τ between them. Each pulse is linearly polarized, but the polarization vector is rotated from one pulse to the next one by the angle δ , such that the whole pulse train rotates with a rotational period $T_{\text{train}} = 2\pi \tau / \delta$ (see Fig. 1). Choosing the laser propagation axis as the z axis, the electric field of the *n*th pulse is given as

$$E_n(t) = \mathcal{E}_n(t)\hat{e}_n \cos(\omega t + \phi), \qquad (1)$$

where $\hat{e}_n = (\cos n\delta, \sin n\delta, 0)$ is the polarization vector, ω is the carrier frequency, and ϕ is the phase. We consider a laser for which the carrier frequency is far detuned from any electronic or vibrational resonance. The laser pulses therefore interact with the molecules via Raman-type excitations of the rotational levels. The envelope of the electric field is given as

$$\mathcal{E}_n(t) = E_n \exp[-(t - n\tau)^2 / (2\sigma^2)].$$
 (2)

Here, σ determines the pulse duration.

The nonresonant laser pulse induces a dipole in the molecule via its electric polarizability and then interacts with this induced dipole. Averaging over the fast oscillations of the



FIG. 1. (Color online) Sketch of the considered scenario: A train of linearly polarized laser pulses interacts with linear molecules. The polarization axis is rotated by an angle δ between each pulse, and the time delay τ between the pulses is constant.

electric field, we arrive at the effective interaction potential [39]

$$V = -\frac{1}{4} \sum_{n} \mathcal{E}_{n}^{2}(t) (\Delta \alpha \cos^{2} \beta_{n} + \alpha_{\perp}).$$
(3)

Here, $\Delta \alpha = \alpha_{\parallel} - \alpha_{\perp}$ is the polarizability anisotropy of the molecule, where α_{\parallel} and α_{\perp} are the polarizabilities along and perpendicular to the molecular axis, respectively. The angle β_n is the angle between the molecular axis and the polarization direction of the *n*th pulse. The last term in Eq. (3), α_{\perp} , is independent of the molecular orientation and does not influence the rotational dynamics. We will therefore omit it in the following.

It is convenient to introduce an effective pulse strength P, which corresponds to the typical amount of angular momentum (in units of \hbar) transferred to the molecule by the pulse. For a single pulse, it is defined as

$$P = \frac{\Delta\alpha}{4\hbar} \int dt \mathcal{E}^2(t) = \frac{\Delta\alpha I_{\text{peak}} \sigma \sqrt{\pi}}{2c\epsilon_0 \hbar}.$$
 (4)

Here, I_{peak} is the peak intensity of the pulse, c is the speed of light, and ϵ_0 is the vacuum permittivity.

In this work, we consider two kinds of pulse trains. The first one is a train of N equally strong pulses, such that the effective interaction strength P_n of the *n*th pulse is given as

$$P_n = P_{\rm tot}/N,\tag{5}$$

where $P_{\text{tot}} = \sum P_n$ is the total strength of the whole pulse train. Such a pulse train can be generated, e.g., by nested interferometers [40,41]. The second kind is trains like the ones used in the experiments [37,38], which were created by pulse-shaping techniques. In this case, the effective interaction strength of the *n*th pulse is given as

$$P_n = P_{\text{tot}} J_n^2(A), \tag{6}$$

where J_n is the Bessel function of the first kind and A is a parameter. Since $J_n(x) \ll 1$ for |n| > |x|, this train contains about 2A + 1 nonzero pulses. In Fig. 2 we depict the intensity envelope of the train for different values of A.

B. Numerical treatment

1. Nitrogen

At first we consider molecular nitrogen as an example of a simple linear molecule. Since the laser pulses are assumed to be far off-resonant from electronic or vibrational transitions, it is sufficient to consider only the rotational excitation in



FIG. 2. Effective interaction strengths for a train with modulated intensities as described by Eq. (6). The total interaction strength is $P_{\text{tot}} = 1$.

the vibronic ground state. The rotational eigenfunctions are the spherical harmonics $|J, M\rangle$. Here, J is the total angular momentum, and M is its projection on the Z axis, which we have chosen to be along the laser propagation direction. Note that for N₂ in its electronic ground state, the total angular momentum **J** is equal to the orbital angular momentum **O** of the rotation of the nuclei. Although we are interested in the latter, for simplicity we keep to the more common notation using the total angular momentum **J**. The rotational levels are given as $E_J = BJ(J + 1) - DJ^2(J + 1)^2$, where *B* is the rotational constant and *D* is the centrifugal distortion constant.

For the numerical treatment of the problem it is convenient to express the wave function as a linear combination of the rotational eigenfunctions:

$$|\Psi(t)\rangle = \sum_{J,M} C_{J,M}(t) e^{-iE_J t/\hbar} |J,M\rangle.$$
(7)

Inserting expansion (7) and interaction potential (3) into the time-dependent Schrödinger equation,

$$i\hbar \frac{\partial |\Psi(t)\rangle}{\partial t} = \hat{H}(t)|\Psi(t)\rangle,$$
 (8)

we obtain

$$i\hbar \sum_{J',M'} \frac{\partial C_{J'M'}(t)}{\partial t} e^{-iE_{J'}t/\hbar} |J',M'\rangle$$

=
$$\sum_{J',M'} C_{J'M'}(t) e^{-iE_{J'}t/\hbar} V(t) |J',M'\rangle.$$
(9)

Multiplying from the left by $\frac{1}{i\hbar}\langle J, M|e^{iE_Jt/\hbar}$, we obtain a set of coupled differential equations for the expansion coefficients $C_{J,M}(t)$:

$$\frac{\partial C_{JM}(t)}{\partial t} = \frac{1}{i\hbar} \sum_{J',M'} C_{J'M'}(t) e^{-i(E_{J'}-E_J)t/\hbar} \langle J,M|V(t)|J',M'\rangle$$
$$= i \frac{\Delta \alpha}{4\hbar} \sum_{n=-\infty}^{+\infty} \mathcal{E}_n^2(t) \sum_{J',M'} C_{J'M'}(t) e^{-i(E_{J'}-E_J)t/\hbar}$$
$$\times \langle J,M|\cos^2\beta_n|J',M'\rangle.$$
(10)

Here, β_n is the angle between the molecular axis and the polarization direction of the *n*th pulse.

The matrix element $\langle J, M | \cos^2 \beta_n | J', M' \rangle$ is obtained as follows. First, $\cos^2 \beta_n$ is expressed as

$$\cos^{2} \beta_{n} = \cos^{2}(n\delta) \sin^{2} \theta \cos^{2} \phi + \sin^{2}(n\delta) \sin^{2} \theta \sin^{2} \phi + \frac{1}{2} \sin(2n\delta) \sin^{2} \theta \sin(2\phi), \qquad (11)$$

where θ and ϕ are the polar and azimuthal angles of the molecular axis, respectively. Then, we express $\cos^2 \beta_n$ in terms of the Wigner rotation matrices [42] $D_{MN}^{(J)}$ as

$$\cos^{2}\beta_{n} = \frac{1}{3} - \frac{1}{3}D_{00}^{(2)*} + \frac{1}{\sqrt{6}}e^{i2n\delta}D_{-20}^{(2)*} + \frac{1}{\sqrt{6}}e^{-i2n\delta}D_{20}^{(2)*}.$$
(12)

Here, we use the relations

$$\sin^2\theta\cos^2\phi = \frac{1}{\sqrt{6}} \left(D_{20}^{(2)*} + D_{-20}^{(2)*} \right) - \frac{1}{3} D_{00}^{(2)*} + \frac{1}{3},$$
(13a)

$$\sin^2 \theta \sin^2 \phi = -\frac{1}{\sqrt{6}} \left(D_{20}^{(2)*} + D_{-20}^{(2)*} \right) - \frac{1}{3} D_{00}^{(2)*} + \frac{1}{3},$$
(13b)

$$\sin^2\theta\sin(2\phi) = -i\sqrt{\frac{2}{3}} \left(D_{20}^{(2)*} - D_{-20}^{(2)*} \right).$$
(13c)

Finally, by using [42]

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$$\langle J, M | D_{M_00}^{(2)*} | J', M' \rangle = (-1)^M \sqrt{(2J+1)(2J'+1)} \\ \times \begin{pmatrix} J & 2 & J' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} J & 2 & J' \\ -M & M_0 & M' \end{pmatrix},$$
(14)

where the brackets denote the Wigner 3j symbol, we obtain the matrix element $\langle J, M | \cos^2 \beta | J', M' \rangle$. Note that only levels with $\Delta J = 0, \pm 2, \pm 4, \ldots$ and $\Delta M = 0, \pm 2, \pm 4, \ldots$ are coupled.

In our simulations, we solve Eq. (10) numerically. We do ensemble averaging by solving Eq. (10) for different initial states $|\Psi_{\text{initial}}\rangle = |J_0, M_0\rangle$ and weighting the result by the Boltzmann factor of the initial state. Note that the Boltzmann factor includes a degeneracy factor arising from nuclear-spin statistics [43]. For example, the nitrogen isotope ¹⁵N has a nuclear spin of I = 1/2. Therefore, the diatomic molecule ¹⁵N₂ can have a total nuclear spin of I = 1 (ortho-nitrogen) or I = 0 (para-nitrogen). The former has three degenerate nuclear-spin wave functions, which are symmetric with respect to an exchange of the two nuclei, and the latter has one antisymmetric nuclear-spin wave function. Due to the fermionic nature of ¹⁵N, the total wave function of the molecule has to be antisymmetric with respect to the exchange of the nuclei. Therefore, ortho- and para-nitrogen can be distinguished by their rotational wave functions: Ortho-nitrogen is only found with odd angular momentum J, para-nitrogen is only found with even angular momentum J, and the ratio of even to odd states is 1:3 due to the degeneracy of the nuclear-spin wave functions of ortho-nitrogen. For ¹⁴N with a nuclear spin of I = 1, there are three nuclear-spin isomers, two with symmetric nuclear-spin wave functions (one of them fivefold degenerate) and one with threefold degenerate antisymmetric



FIG. 3. The lowest rotational levels of ${}^{16}O_2$ in its electronic and vibrational ground states. The energies are given in cm⁻¹. Also shown are the allowed transitions between these levels induced by the laser pulse (3).

nuclear-spin wave functions. The resulting ratio of even to odd rotational states is 2:1.

2. Oxygen

Molecular oxygen has a more complex rotational spectrum than simple diatomic molecules such as nitrogen or hydrogen [42,44]. The electronic ground state is a ${}^{3}\Sigma_{g}^{-}$ state, so the total electronic spin S is nonzero. This gives rise to spin-spin and spin-orbit coupling, and therefore the total angular momentum J does not solely describe the nuclear rotational motion as for N₂, which has a ${}^{1}\Sigma_{\rho}^{+}$ electronic ground state. In particular, J = N + S, where N is the orbital angular momentum; since the electronic orbital angular momentum is zero, N is identical to **O**, the nuclear orbital angular momentum. The rotational quantum number J can take the values J = N + S, N + S - S $1, \ldots, N - S$. Therefore, for oxygen in its vibronic ground state with S = 1, each level N is split into three levels with J =N - 1, N, N + 1, as is shown in Fig. 3. The splitting is stronger for low values of N. Additionally, for symmetry reasons, only odd values are allowed for N [42].

For the numerical treatment, we express the wave function as a linear combination of Hund's case b basis states [42,44]:

$$|\Psi\rangle = \sum_{JNM} C_{JNM}(t) e^{-iE_{JN}t/\hbar} |\eta\Lambda; N\Lambda; NSJM\rangle.$$
(15)

Here, Λ is the projection of the electronic angular momentum on the molecular axis, N is the orbital angular momentum, S is the electronic spin, J is the total angular momentum, M is the projection of the total angular momentum on the Z axis, and η is a combined quantum number of the remaining vibronic quantum numbers. E_{JN} are the energies of the rotational states; see Fig. 3. As before, we assume that the molecules are initially in their vibronic ground state. Since the interaction does not induce any vibronic transitions, it is independent of η , and furthermore $\Lambda = 0$ and S = 1 are constant. For ease of reading, in the following we denote the eigenstates in short as $|\eta\Lambda; N\Lambda; NSJM \rangle \equiv |JNM \rangle$.

As before, we insert the expanded wave function (15) into the time-dependent Schrödinger equation and obtain a system of differential equations for the expansion coefficients C_{JNM} :

$$\frac{\partial C_{JNM}(t)}{\partial t} = i \frac{\Delta \alpha}{4\hbar} \sum_{n=-\infty}^{+\infty} \mathcal{E}_n^2(t) \\ \times \sum_{J',N',M'} C_{J'N'M'}(t) e^{-i(E_{J'N'} - E_{JN})t/\hbar} \\ \times \langle J, N, M | \cos^2 \beta_n | J', N', M' \rangle.$$
(16)

The matrix elements $\langle JNM | \cos^2 \beta | J'N'M' \rangle$ are determined as follows. First, we use Eq. (12) to replace $\cos^2 \beta$, which yields

$$\begin{aligned} \langle JNM | \cos^{2} \beta | J'N'M' \rangle \\ &= \frac{1}{3} \langle JNM | J'N'M' \rangle - \frac{1}{3} \langle JNM | D_{00}^{(2)*} | J'N'M' \rangle \\ &+ \frac{1}{\sqrt{6}} e^{i2n\delta} \langle JNM | D_{-20}^{(2)*} | J'N'M' \rangle \\ &+ \frac{1}{\sqrt{6}} e^{-i2n\delta} \langle JNM | D_{20}^{(2)*} | J'N'M' \rangle. \end{aligned}$$
(17)

We now have to determine the value of $\langle \Lambda NSJM | D_{M_0}^{(2)*} | \Lambda N'SJ'M' \rangle$. Here we explicitly write down all quantum numbers (apart from η). We use the Wigner-Eckart theorem (see, e.g., [42]) to exclude the dependence on the molecular orientation:

$$\langle \Lambda NSJM | D_{M_00}^{(2)*} | \Lambda N'SJ'M' \rangle$$

$$= (-1)^{J-M} \begin{pmatrix} J & 2 & J' \\ -M & M_0 & M' \end{pmatrix}$$

$$\times \langle \Lambda NSJ | | D_{.0}^{(2)*} | | \Lambda N'SJ' \rangle,$$
(18)

where the parentheses are the Wigner 3j symbol. The dot in the subscript of the rotation matrix indicates that this matrix element is reduced regarding the orientation in the space-fixed coordinate system [42]. Next, we use the fact that $D_{.0}^{(2)*}$ does not act on the electronic spin so that we can exclude *S* from the matrix element as well and obtain [42]

$$\langle \Lambda N S J || D_{.0}^{(2)*} || \Lambda N' S J' \rangle$$

$$= (-1)^{J'+N+2+S} \sqrt{(2J+1)(2J'+1)}$$

$$\times \begin{cases} N' & J' & S \\ J & N & 2 \end{cases} \langle \Lambda N || D_{.0}^{(2)*} || \Lambda N' \rangle.$$
(19)

Here, the curly brackets denote the Wigner 6j symbol. Finally, the reduced matrix element in Eq. (19) is given as

$$\langle \Lambda N || D_{.0}^{(2)*} || \Lambda N' \rangle$$

= $(-1)^{N-\Lambda} \sqrt{(2N+1)(2N'+1)} \begin{pmatrix} N & 2 & N' \\ -\Lambda & 0 & \Lambda \end{pmatrix}.$ (20)

Here, we used Eq. (5.186) in Ref. [42] and applied it for Hund's case b. We insert now S = 1 and $\Lambda = 0$ and obtain the matrix

elements of the rotation matrices as

$$\langle \Lambda NSJM | D_{M_00}^{(2)*} | \Lambda N'SJ'M' \rangle$$

$$= \sqrt{(2J+1)(2J'+1)(2N+1)(2N'+1)} \\ \times \begin{pmatrix} J & 2 & J' \\ -M & M_0 & M' \end{pmatrix} \begin{pmatrix} N & 2 & N' \\ 0 & 0 & 0 \end{pmatrix} \\ \times \begin{cases} N' & J' & 1 \\ J & N & 2 \end{cases} (-1)^{J+J'-M+1}.$$

$$(21)$$

Inserting Eq. (21) into (17) yields the matrix elements $\langle JNM | \cos^2 \beta | J'N'M' \rangle$. In order to lower the numerical effort, we treat the pulses as δ pulses (sudden approximation); i.e., we neglect the molecular rotation during each pulse. Comparison with experiment [37] shows that this approximation is well justified for pulses of a duration of 500 fs. Using the method of an artificial time parameter ξ as described in Ref. [9], the differential equations for the expansion coefficients for a single laser pulse become

$$\frac{\partial C_{JNM}(\xi)}{\partial \xi} = i P_n \sum_{J', N'M'} C_{J'N'M'}(\xi) \\ \times \langle J, N, M | \cos^2 \beta_n | J', N', M' \rangle, \quad (22)$$

where P_n is the effective interaction strength introduced above. Setting $C_{JNM}(\xi = 0)$ to the values just before the pulse, we obtain the expansion coefficients right after the pulse as $C_{JNM}(\xi = 1)$ [9]. To obtain the final expansion coefficients after the whole pulse train, we solve Eq. (22) for every pulse, letting the wave packet (15) evolve freely between the pulses. To account for thermal effects, we do ensemble averaging over the initial state. Since ¹⁶O has a nuclear spin of I = 0, there are no degeneracies due to the nuclear-spin wave functions. However, only odd values are allowed for the orbital angular momentum N.

III. RESULTS

We will first present the results for excitation of nitrogen molecules by a train of equally strong pulses. We will then demonstrate how such pulse trains can be used to selectively excite isotopologs and nuclear-spin isomers in molecular mixtures. Finally, we will show results for the excitation of the more complex oxygen molecules by a train of unequal pulses [given by Eq. (6)] in order to compare our results with recent experiments [37,38].

We define the final population Q(J) of a rotational level J as

$$Q(J) = \sum_{i} g_{i} \sum_{M} |C_{i,JM}|^{2}.$$
 (23)

Here, *i* denotes the initial state, and g_i is its statistical weight. We also define the directionality $\epsilon(J)$ of the excited wave packet as

$$\epsilon(J) = \frac{Q_L(J) - Q_R(J)}{Q_L(J) + Q_R(J)},\tag{24}$$

where $Q_L(J)$ and $Q_R(J)$ are the counterclockwise-rotating and the clockwise-rotating fractions of the population of the level J,

$$Q_L(J) = \sum_{i} g_i \left(\sum_{M>0} |C_{i,JM}|^2 + 1/2 |C_{i,J0}|^2 \right), \quad (25a)$$

$$Q_R(J) = \sum_i g_i \left(\sum_{M < 0} |C_{i,JM}|^2 + 1/2 |C_{i,J0}|^2 \right).$$
(25b)

Note that half of the population of the states with M = 0 is apportioned to clockwise rotation and half to counterclockwise rotation. A positive (negative) $\epsilon(J)$ indicates a preferentially counterclockwise (clockwise) rotation.

A. Excitation of nitrogen molecules with a train of equally strong pulses

In the following, we show the results for ${}^{14}N_2$ molecules interacting with a train of eight equally strong pulses with durations of $\sigma = 30$ fs [see Eq. (2)] and a total interaction strength of $P_{tot} = 5$. The peak intensity of a single pulse is therefore approximately 3×10^{12} W/cm². The pulse duration is well below the rotational periods of the highest expected excitations (remember that *P* corresponds to the typical angular momentum in the units of \hbar transferred by the pulse). The molecules are considered to be initially at a temperature of T = 8 K. At this temperature there is a considerable initial (thermal) population in the level J = 2, with $Q_{th}(2) = 0.25$. Also in J = 3 there is some initial population, $Q_{th}(3) = 0.02$. The levels J = 4 and J = 5 are not populated (note that due to nuclear-spin statistics, two-thirds of the population are found in the even levels and one-third is found in the odd ones).

In Fig. 4 the population Q(J) is shown for the rotational levels J = 2,3,4,5 for ¹⁴N₂ molecules, and Fig. 5 displays the directionality $\epsilon(J)$ for the same levels. The plots show the population and the directionality as a function of the pulse-train period τ and the pulse-to-pulse polarization angle shift δ .

The population plots for all levels show a distinct pattern of diagonal and horizontal lines. These lines are described by the equation

$$\tau = t_{\rm exc}(J) \left(m + \Delta M \frac{\delta}{2\pi} \right).$$
 (26)

Here, *m* is an integer and $\Delta M = 0, \pm 2$ (0 yields the horizontal lines, +2 corresponds to the diagonal lines with a positive slope, and -2 yields the diagonal lines with a negative slope). Furthermore, t_{exc} is the period corresponding to the excitation from level J - 2 to level J and is given as

$$t_{\rm exc}(J) = 2\pi\hbar/(E_J - E_{J-2}) = t_{\rm rev}/(2J-1),$$
 (27)

where $t_{rev} = \hbar \pi / B$ is the rotational revival time (8.38 ps for ¹⁴N₂ in its vibronic ground state).

The directionality plots in Fig. 5 show in general the same structure as the population plots, although now the horizontal lines are missing. Furthermore, we can see that the diagonals with a positive slope correspond to a counterclockwise rotational sense [$\epsilon(J) > 0$], and the diagonals with a negative slope correspond to a clockwise rotation. Also, next to the main diagonals, there is a chessboard pattern visible, especially for higher levels.

The general structure of the population and directionality plots is very similar to experimental observations (Figs. 5



FIG. 4. (Color online) Population Q(J) [see Eq. (23)] of different rotational levels J for ¹⁴N₂ at T = 8 K, after interacting with a train of eight equal pulses. The total interaction strength is $P_{tot} = 5$, and the pulse duration is $\sigma = 30$ fs. The minimum of the color-coding is zero for all panels, and the maximum is 0.6 for (a), 0.25 for (b) and (c), and 0.1 for (d).

and 6 in Ref. [38]), although the latter do not resolve the fine chessboard pattern. It should be noted that in the experiments [38] a train of unequal pulses described by (6) was used, whereas the results presented here are for a train of equally strong pulses.

The structures seen in Figs. 4 and 5 can be explained as the result of the quantum interference of different excitation pathways, as we will show now. For simplicity, we will treat the pulses as δ pulses in the following analysis. This is well justified as the utilized pulse duration of $\sigma = 30$ fs is much shorter than the relevant rotational periods of ¹⁴N₂. The evolution of the wave packet over one period of the pulse train is given by

$$|\Psi(t_{n}^{+})\rangle = e^{iP\cos^{2}\beta_{n}}e^{-i\hat{J}^{2}\tau/(2I\hbar)}|\Psi(t_{n-1}^{+})\rangle, \qquad (28)$$



FIG. 5. (Color online) Directionality $\epsilon(J)$ [see Eq. (24)] of different rotational levels J for ¹⁴N₂ at T = 8 K after interacting with a train of eight equal pulses. The total interaction strength is $P_{\text{tot}} = 5$, and the pulse duration is $\sigma = 30$ fs. Positive ϵ corresponds to counterclockwise rotation; negative ϵ corresponds to clockwise rotation.

where t_n^+ is the time instant right after the *n*th pulse, \hat{J} is the angular momentum operator, and *I* is the moment of inertia. The interaction term can be expressed as

$$e^{iP\cos^{2}\beta_{n}} = \hat{R}(n\delta,\pi/2,0)e^{iP\cos^{2}\theta}\hat{R}^{-1}(0,-\pi/2,-n\delta)$$

= $e^{-in\delta\hat{J}_{z}/\hbar} \underbrace{e^{-i\hat{J}_{y}\pi/(2\hbar)}e^{iP\cos^{2}\theta}e^{i\hat{J}_{y}\pi/(2\hbar)}}_{\hat{W}}e^{in\delta\hat{J}_{z}/\hbar}.$
(29)

Here, \hat{R}^{-1} rotates the basis from the space-fixed system (quantization axis along the laser propagation) to a "pulse-fixed" system (quantization axis along the electric-field polarization of the *n*th pulse). The operator \hat{W} is the same for every pulse. Using (29), we can express the evolution operator that brings

the system from its initial state to the final state after the last pulse as

$$\hat{U} = \prod_{n=1}^{N} e^{-in\delta \hat{J}_{z}/\hbar} \hat{W} e^{in\delta \hat{J}_{z}/\hbar} e^{-i\frac{\hat{J}^{2}}{2\hbar}\tau}.$$
(30)

The probability of the transition from $|J'M'\rangle$ to $|JM\rangle$ is given as $|\langle JM|\hat{U}|J'M'\rangle|^2$. Using the expansion

$$e^{iP\cos^2\theta} = 1 + iP\cos^2\theta - \frac{P^2}{2}\cos^4\theta + \cdots$$
 (31)

we can express the evolution operator as

$$\hat{U} = \prod_{n=1}^{N} e^{-in\delta \hat{J}_{z}/\hbar} e^{-i\hat{J}_{y}\pi/(2\hbar)} \left(1 + iP\cos^{2}\theta + \cdots\right)$$

$$\times e^{i\hat{J}_{y}\pi/(2\hbar)} e^{in\delta\hat{J}_{z}/\hbar} e^{-i\frac{j^{2}}{2\hbar}\tau}$$

$$\approx e^{-i\frac{j^{2}}{2\hbar}\tau N} + iP\sum_{n=1}^{N} e^{-i\frac{j^{2}}{2\hbar}\tau(N-n)} e^{-in\delta\hat{J}_{z}/\hbar}$$

$$\times e^{-i\hat{J}_{y}\pi/(2\hbar)}\cos^{2}\theta e^{i\hat{J}_{y}\pi/(2\hbar)} e^{in\delta\hat{J}_{z}/\hbar} e^{-i\frac{j^{2}}{2\hbar}\tau n}$$
(32)

The approximation in the last line is valid in the limit of weak pulses (P < 1). In the following, we will only consider this limit. Using Eq. (32) as the evolution operator, the total probability for a transition from state $|J'M'\rangle$ to another state, $|JM\rangle$, is given as

$$|\langle JM|\hat{U}|J'M'\rangle|^{2}$$

$$= P^{2} \left| \sum_{n=1}^{N} e^{-i(N-n)E_{J}\tau/\hbar} \langle JM|\hat{V}|J'M'\rangle \right|$$

$$\times e^{-i(M-M')n\delta} e^{-inE_{J'}\tau/\hbar} \right|^{2}$$

$$= P^{2} |\langle JM|\hat{V}|J'M'\rangle|^{2}$$

$$\times \underbrace{\sum_{n,n'=1}^{N} \cos\left[\left(\frac{\Delta E\tau}{\hbar} - \Delta M\delta \right) (n-n') \right]}_{\equiv \Phi}. \quad (33)$$

Here, $\hat{V} = e^{-i\hat{J}_y\pi/(2\hbar)}\cos^2(\theta)e^{i\hat{J}_y\pi/(2\hbar)}$ and $\Delta E = E_J - E_{J'}$. The term Φ , and therefore the transition amplitude, is maximized if the first factor in the argument of the cosine is a multiple of 2π , which yields

$$\tau = \frac{2\pi\hbar}{\Delta E} \left(m + \Delta M \frac{\delta}{2\pi} \right), \tag{34}$$

where m is an integer. This condition is equivalent to (26) and exactly describes the lines in Figs. 4 and 5.

Using these insights, we can now explain the results seen in Figs. 4 and 5. The patterns are the result of quantum interferences of different excitation pathways. These interferences are constructive when condition (34) is fulfilled, causing the lines seen in Figs. 4 and 5. With the help of Eq. (34) we can also see that the horizontal lines are due to transitions with no change of the projection M, i.e., $\Delta M = 0$. There are no horizontal lines in the directionality plots since $\Delta M = 0$ means that there is no change in the sense of the rotation. The diagonals with a positive slope are due to transitions



FIG. 6. (Color online) Sum $|\Phi|$ of the interference terms in Eq. (33) as a function of the detuning *x* from condition (34). The plot shows Φ for three different numbers *N* of pulses, and the result is normalized to N^2 .

with $\Delta M = 2$. The increase of M shifts the rotational sense towards a counterclockwise direction and therefore increases the directionality $\epsilon(J)$. The opposite is found for the diagonals with a negative slope, which correspond to $\Delta M = -2$.

The chessboard pattern seen in the directionality plot can be explained by looking at the sum Φ when τ is detuned from condition (34):

$$\tau = t_{\rm exc} \Delta M \frac{\delta}{2\pi} + x. \tag{35}$$

Here, $t_{\text{exc}} = 2\pi\hbar/\Delta E$. In Fig. 6 we plot Φ as a function of the detuning *x*. It can be seen that next to the main peaks at integer x/t_{exc} , there are weak oscillatory beats in between. The minima of those beats are found at $x/t_{\text{exc}} = m/N$, where *N* is the number of pulses and *m* and *N* are mutually prime. These "sidebands" are weak, and therefore they cannot be seen in the population plots in Fig. 4. On the other hand, the directionality measures the relative difference of the populations, so these weak sidebands become visible if the thermal population of the rotational level is sufficiently small.

From Fig. 6 we can see that an increase of the number of pulses leads not only to an increase in the number of sidebands but also to a narrowing of the main peak of $\Phi(x)$. Therefore, we expect a narrowing of the lines seen in the population plots for larger *N*. This can be seen in Fig. 7 for the population of the levels J = 2 and J = 3. Here, we use the same parameter values as in Fig. 4 but twice as many pulses while keeping the total interaction strength P_{tot} constant. A similar effect of the narrowing of the resonance when increasing the number of pulses was already found for the quantum resonance at the full rotational revival [33].

B. Selective excitation

1. Nuclear-spin isomer-selective excitation

The nitrogen isotopolog ${}^{15}N_2$ can be found as orthonitrogen with a total nuclear spin of I = 1 or as paranitrogen with a total nuclear spin of I = 0. These spin isomers can be distinguished by their rotational wave functions [43]: Ortho-nitrogen is only found with odd angular



FIG. 7. (Color online) Population Q(J) [see Eq. (23)] of the rotational levels J = 2 and J = 3 for ¹⁴N₂ at T = 8 K after interacting with a train of 16 equal pulses. The total interaction strength is $P_{\text{tot}} = 5$, and the pulse duration is $\sigma = 30$ fs.

momentum J; para-nitrogen is only found with even angular momentum J.

In Fig. 8 we show the final population for the lowest rotational levels after excitation by a pulse train with $\delta = 0$ and period τ close to one quarter of the revival time (marked by the dashed line). By tuning the time delay between the pulses one can choose which state is excited the strongest. Moreover, for $\tau < t_{rev}/4$ only odd levels are significantly excited, whereas for



FIG. 8. (Color online) Final population of the rotational levels of ¹⁵N₂ after interaction with 8 equal pulses with a duration of $\sigma = 30$ fs and a nonrotating polarization ($\delta = 0$) and $P_{tot} = 5$ at T = 8 K. Each curve is normalized to its maximum. The dashed line indicates the quarter revival time $t_{rev}/4$. For τ slightly smaller than $t_{rev}/4$, only odd states are excited; for τ slightly larger, only even states are excited.



FIG. 9. (Color online) Selective excitation of the nuclear-spin isomers of ¹⁵N₂ by interaction with a periodic pulse train of eight equally strong pulses with a duration of $\sigma = 30$ fs. The molecules are initially at T = 8 K. The total interaction strength is $P_{\text{tot}} = 5$. The results are shown as a function of the pulse-train period τ . (a) Absorbed rotational energy for a nonrotating ($\delta = 0$) pulse train. (b) Projection of the molecular angular momentum on Z for a rotating ($\delta = \pi/4$) pulse train. The angular momentum is given in units of \hbar . The dashed vertical lines indicate quarter, half, three-quarter, and full rotational revival times.

 $\tau > t_{rev}/4$ only even levels are significantly excited. Therefore, by choosing τ slightly smaller (slightly larger) than $t_{rev}/4$, one selectively excites ortho-nitrogen (para-nitrogen). This effect is shown in Fig. 9(a), which displays the absorbed energy for both spin isomers. One can see separate peaks for both isomers, in particular close to $\tau = t_{rev}/4$ and $\tau = 3t_{rev}/4$. This selective excitation of spin isomers around a quarter of the revival time was demonstrated in a recent experiment [32].

At $\delta \neq 0$, one may use chiral pulse trains to bring different spin isomers to a rotation of opposite sense. The best selectivity is achieved for $\delta = \pi/4$. In particular, at $\delta = \pi/4$ and $\tau = t_{rev}/4$ all excited even states have a positive directionality, and all excited odd states have a negative directionality. The reverse is found at $\tau = 3t_{rev}/4$. The opposite directionality of even and odd rotational states at $\tau = t_{rev}/4$ and $\tau = 3t_{rev}/4$ was also demonstrated experimentally (see Fig. 7 in Ref. [38]). This effect allows for spin isomer-selective excitation, as shown in Fig. 9(b). Here, the projection of the angular momentum on the z axis is shown for both spin isomers. For $\tau = t_{rev}/4$, ortho-nitrogen exhibits counterclockwise rotation, whereas para-nitrogen rotates clockwise. The opposite is found at $\tau = 3t_{rev}/4$.



FIG. 10. (Color online) Selective excitation of the nitrogen isotopologs ¹⁴N₂ and ¹⁵N₂ by interaction with a periodic pulse train of eight equally strong pulses with a duration of $\sigma = 30$ fs. The molecules are initially at T = 8 K. The total interaction strength is $P_{\text{tot}} = 5$. The results are shown as a function of the pulse-train period τ . (a) Absorbed rotational energy for a nonrotating ($\delta = 0$) pulse train. (b) Projection of the molecular angular momentum on Z for a rotating ($\delta = \pi/4$) pulse train. The angular momentum is given in units of \hbar . The shaded areas mark time delays for which the two isotopologs rotate in opposite directions after the excitation.

2. Isotopolog-selective excitation

Isotopologs are chemically identical molecules with a different isotopic composition, e.g., ${}^{14}N_2$ and ${}^{15}N_2$. Due to the different moments of inertia, isotopologs have different rotational time scales. For example, ${}^{14}N_2$ has a rotational revival time of $t_{rev} = 8.38$ ps, whereas for ${}^{15}N_2$ the revival time is $t_{rev} = 8.98$ ps. Using the fact that the rotational excitation is strongest if the pulse-train period τ equals the rotational revival time, we can selectively excite ${}^{14}N_2$ and ${}^{15}N_2$ by tuning the train period to $\tau = 8.38$ ps and $\tau = 8.98$ ps, respectively [33,38]. In Fig. 10(a) we show the absorbed rotational energy of the two nitrogen isotopologs after interaction with a nonrotating ($\delta = 0$) pulse train, and one can clearly see the selective excitation at the respective revival times.

Inducing counterrotation of different isotopologs is more challenging. For spin isomers the time scales were identical, and one could use the different directionality of even and odd states for $\tau = t_{rev}/4$ to induce counterrotation. For isotopologs the time scales are different. Counterrotation can only be excited if for some set of parameters the pulse train accidentally excites rotation of opposite direction in the isotopologs. For ¹⁴N₂ and ¹⁵N₂ three such regions can be seen in Fig. 10(b) (see shaded region): At $\tau \approx 2.2$ ps and $\tau \approx 7.65$ ps the heavier isotopolog rotates predominantly counterclockwise ($\langle J_z \rangle > 0$), and the lighter isotopolog rotates mainly clockwise; at $\tau \approx 8.65$ ps the opposite is found.

C. Oxygen molecules in a chiral pulse train

As a special example, we now consider the excitation of oxygen molecules by a chiral pulse train. Instead of identical pulses we consider the more complex pulse sequence (6), corresponding to the one used in experiment [37] (see Fig. 2). We also use parameters corresponding to this experiment: The total interaction strength is $P_{\text{tot}} = 7.5$, and A = 2 [see Eq. (6)]. Therefore, the strongest pulse in the train has an effective interaction strength of P = 2.5, which corresponds to a peak intensity of approximately 8×10^{12} W/cm². Due to the higher numerical complexity of the problem, we only considered δ pulses. Comparison with experiments [37] shows that this approximation is well justified.

Unlike molecular nitrogen, oxygen has a nonzero total electronic spin in its ground state. There is a coupling between the electronic spin and the orbital angular momentum, leading to splitting of the rotational levels, as shown in Fig. 3. Also, the orbital angular momentum N is not identical to the total angular momentum J any longer, but J = N - 1, N, N + 1. Note that due to the symmetry of the molecule, only odd values are permitted for N.

For oxygen, we define the population Q(N) of a rotational level N as

$$Q(N) = \sum_{i} g_{i} \sum_{J=N-1}^{N+1} \sum_{M=-J}^{J} |c_{i,JNM}|^{2}.$$
 (36)

Here, *i* denotes the initial state, and g_i is the corresponding statistical weight. The populations of counterclockwise-rotating states $Q_L(N)$ and clockwise-rotating states $Q_R(N)$ are given as

$$Q_L(N) = \sum_i g_i \left(\sum_{J,M>0} |c_{i,JNM}|^2 + 1/2 |c_{i,JN0}|^2 \right), \quad (37a)$$

$$Q_R(N) = \sum_i g_i \left(\sum_{J,M<0} |c_{i,JNM}|^2 + 1/2|c_{i,JN0}|^2 \right).$$
(37b)

The directionality of the states with given N is defined as

$$\epsilon(N) = \frac{Q_L(N) - Q_R(N)}{Q_L(N) + Q_R(N)}.$$
(38)

In Fig. 11 we show the final population of the rotational levels N = 3 and N = 5 after interaction with the pulse train. In Fig. 12 the directionality of these levels is shown. We can see the same basic line structure as before for the nitrogen molecules. However, due to the different pulse train and because of the level splitting, the lines are broader, and the pattern becomes more complex, especially for larger values of τ . On the other hand, the chessboard pattern seen in the directionality plots for molecular nitrogen is not found for molecular oxygen. This is due to the fact that the chessboard pattern is caused by very weak sidebands, which do not exist for molecular oxygen due to the level splitting. One can also see that the plots for level N = 3 look more complex than



FIG. 11. (Color online) Population Q(N) [see Eq. (36)] of the rotational levels N = 3 and N = 5 for ${}^{16}O_2$ at T = 8 K after interacting with a train of δ pulses with the intensity envelope given by (6) (A = 2). The total interaction strength is $P_{\text{tot}} = 7.5$. Note the different scales for the ordinates.

the plots for level N = 5. This is caused by the relatively stronger splitting for lower rotational levels. Our calculated results resemble the ones from experiment [37] very well.



FIG. 12. (Color online) Directionality $\epsilon(N)$ [see Eq. (38)] of the rotational levels N = 3 and N = 5 for ¹⁶O₂ at T = 8 K after interacting with a train of δ pulses with the intensity envelope given by (6) (A = 2). The total interaction strength is $P_{\text{tot}} = 7.5$. Note the different scales for the ordinates.

IV. CONCLUSIONS

In this paper, we provided a detailed theoretical analysis of molecular rotational excitation by a chiral pulse train, which was introduced in Ref. [37] and is presented in more detail in the accompanying experimental paper [38]. The chiral pulse train is formed by linearly polarized pulses, uniformly separated in time by a time delay τ , with a constant pulse-to-pulse angular shift δ of the polarization direction. We showed that for certain combinations of τ and δ molecular rotation with a strong preferential rotational sense (clockwise or counterclockwise) can be excited. In two-dimensional plots of the excited population and the rotational directionality as a function of the pulse-train period and the pulse-to-pulse polarization shift, a distinct pattern is found. It is made out of diagonal lines along which a strong preferential rotational sense is achieved. Our analysis shows that this pattern is caused by quantum interferences of different excitation pathways, which interfere constructively along the above-mentioned lines.

We demonstrated the feasibility for selective excitation of nuclear-spin isomers and isotopologs in a mixture by the chiral pulse train. We demonstrated the selectivity using para-nitrogen and ortho-nitrogen as an example. By choosing the parameters of the chiral pulse train such that they address only the states of certain parity, one can selectively excite one of the isomers. Since for the chiral pulse train one can also influence the direction of the molecular rotation, it is even possible to induce counterrotation of different nuclear-spin isomers. Selective excitation of isotopologs can be reached by making use of the different rotational time scales of different isotopologs. The pulse-train parameters can be chosen such that they lead to strong excitation of a preferable isotopolog. For other isotopologs in the mixture, the same pulse train most likely leads to a destructive interference of different excitation pathways, so these isotopologs are at best only weakly excited. Spin isomer- and isotopolog-selective excitation using the chiral pulse train was recently shown in experiments [32,38], demonstrating a good agreement with our theoretical analysis.

Finally, we investigated the excitation of the more complex ${}^{16}O_2$ molecule by the chiral pulse train. For this molecule, the rotational levels are split due to spin-spin and spin-orbit interactions. We also used a slightly more complex pulse train as employed in experiment [37]. In spite of these complications, our main conclusions remain valid also for the oxygen molecule.

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