Control of Molecular Rotation with a Chiral Train of Ultrashort Pulses

S. Zhdanovich,¹ A. A. Milner,¹ C. Bloomquist,¹ J. Floß,² I. Sh. Averbukh,² J. W. Hepburn,¹ and V. Milner¹

¹Department of Physics and Astronomy and The Laboratory for Advanced Spectroscopy and Imaging Research (LASIR),

The University of British Columbia, Vancouver, Canada

²Department of Chemical Physics, The Weizmann Institute of Science, Rehovot, Israel

(Received 22 August 2011; published 9 December 2011)

Trains of ultrashort laser pulses separated by the time of rotational revival (typically, tens of picoseconds) have been exploited for creating ensembles of aligned molecules. In this work we introduce a chiral pulse train—a sequence of linearly polarized pulses with the polarization direction rotating from pulse to pulse by a controllable angle. The chirality of such a train, expressed through the period and direction of its polarization rotation, is used as a new control parameter for achieving selectivity and directionality of laser-induced rotational excitation. The method employs chiral trains with a large number of pulses separated on the time scale much shorter than the rotational revival (a few hundred femtosecond), enabling the use of conventional pulse shapers.

DOI: 10.1103/PhysRevLett.107.243004

PACS numbers: 32.80.Qk, 42.50.Ct

Control of molecular rotation with strong nonresonant laser fields has become a powerful tool for creating ensembles of aligned [1–4], oriented [3,5,6], and spinning molecules [7–10]. Numerous applications of rotational control in molecular systems include control of chemical reactions [2,11], deflection of neutral molecules by external fields [12–14], high harmonic generation [15,16], and control of molecular collisions with atoms [17] and surfaces [18–22]. Alignment of molecular axes has been implemented with transform-limited and shaped laser pulses using various approaches (see, e.g., [1,2,23-26]). Increasing the degree of molecular alignment has been achieved by employing a sequence of laser pulses (a "pulse train"), separated by the time of rotational revival [27–29]. Such timing ensures that the accumulative effect of consecutive pulses is equally efficient for all molecules in the ensemble, regardless of their angular momentum.

Creating molecular ensembles with a preferred direction of rotation has been reported in both adiabatic ("optical centrifuge") [7,30-33] and nonadiabatic [8,9] regimes of excitation using a pair of laser pulses with different polarization. In this work we demonstrate an alternative way of exciting unidirectional rotational motion with a "chiral pulse train," in which the polarization of the excitation field rotates from pulse to pulse by a controllable angle, in either clockwise or counterclockwise direction. The time delay between the pulses is much shorter than the revival period. We show that by varying the train parameters using the technique of polarization shaping [34,35], one can achieve selectivity in the rotational excitation and control its directionality. By matching the rotational period of the field polarization to the period of molecular rotation, molecules in a particular angular momentum state can be excited more efficiently than others. The chirality and the period of the pulse train define the direction of rotation.

Our experimental setup is depicted in Fig. 1. Cold molecules are produced by a supersonic expansion of pure oxygen in a vacuum chamber. The rotational temperature of the molecules in the beam is 7–9 K. The molecular beam enters the detection chamber through a 1-mm diameter skimmer. Pump pulses for rotational excitation are produced by a femtosecond Ti:sapphire amplifier (120 fs, 2 mJ at 800 nm and 1 kHz repetition rate) and a homemade pulse shaper based on a liquid crystal spatial light modulator. The pulse length is much shorter than the rotational period of oxygen in the lower rotational states considered in this work. The rotational distribution is probed by narrow band nanosecond pulses generated by a tunable dye laser (3 mJ at 285 nm and 10 Hz repetition rate). The molecules are ionized via a "2 + 1" resonance enhanced multiphoton ionization (REMPI) process, with a two-photon resonant transition $C^3 \prod_g (v'=2) \leftarrow X^3 \Sigma_g^- \times$ (v''=0) of O₂. The total ion signal is detected by a multichannel plate in a standard time-of-flight detection apparatus. Pump and probe beams are combined on a



FIG. 1 (color online). Diagram of the experimental setup. See text for details.

dichroic mirror and focused on the molecular beam with a 150 mm focal length lens. To measure the directionality of molecular rotation with high accuracy and low susceptibility to the power fluctuations of the nanosecond dye laser, a Pockels cell is used to alternate circular polarization of the consecutive probe pulses between left and right. A molecular state with a certain value M_I of the projection of its total angular momentum on the laser beam axis is coupled to the ionization continuum by a left circularly polarized probe field with an equal strength to that of a right circular polarization acting on a state with an opposite projection $-M_I$. Hence, the difference in the ionization rate between left and right circularly polarized probe pulses reflects the asymmetry in the M distribution, or equivalently, the directionality of the induced rotation [8]. In order to reduce the ionization background from pump pulses, the position of the pump beam is shifted by a few hundred μm upstream with respect to the probe beam, while the time delay between the pulses is set to let the excited molecules reach the probe focal spot. We estimate the intensity of pump pulses of the order of 10^{13} W/cm², which results in a dimensionless spatially averaged "rotational kick strength" of $P \approx 7$. The latter parameter characterizes the amount of angular momentum (in units of \hbar) transferred from the laser field to the molecule [3.27].

An example of a chiral pulse train used in this work is shown in Fig. 2. It is produced by a spectral pulse shaper implemented in a standard 4*f* geometry with a doublelayer spatial light modulator in its Fourier plane [36]. The two shaper masks control the spectral phase $\varphi_{1,2}(\omega)$ of the two polarization components of an input pulse along the two orthogonal axes of the shaper, \hat{e}_1 and \hat{e}_2 . If $\varphi_{1,2}(\omega) = A \sin[(\omega - \omega_0)\tau + \delta_{1,2}]$, where ω_0 is the optical carrier frequency, *A* is the modulation amplitude, τ is the train period, and $\delta_{1,2}$ are two arbitrary angles, the resulting field is

$$E(t) = \sum_{i=1,2} \hat{e}_i (\hat{e}_i \cdot \hat{e}_{in}) \sum_{n=-\infty}^{\infty} J_n(A) \varepsilon(t+n\tau) \cos[\omega_0 t + n\delta_i],$$
(1)

where $\varepsilon(t)$ is the electric field envelope of the original pulse polarized along \hat{e}_{in} . Equation (1) describes a train



FIG. 2 (color online). Example of an intensity envelope and polarization of a chiral pulse train implemented in this work. Linear polarization of each pulse is shown in the circles above.

of elliptically polarized pulses, with the polarization ellipticity of the *n*th pulse defined by the phase difference $n(\delta_1 - \delta_2)$. A quarter-wave plate, oriented along \hat{e}_{in} , converts this elliptical polarization back to linear, rotated by an angle $n(\delta_1 - \delta_2)/2$ with respect to the input polarization. By choosing $\delta_1 = -\delta_2 = \delta$, we can create a pulse train with the polarization of each pulse rotated with respect to the previous one by angle δ . The period of the polarization rotation is $T_p = 2\pi\tau/\delta$. In Fig. 2 an example of a pulse train is shown for the modulation amplitude A = 2, train period $\tau = 1$ ps, and polarization rotation period $T_p = 8$ ps. We experimentally characterized the train by polarization sensitive cross-correlation technique [37].

The observed REMPI spectrum of cold oxygen is shown in Fig. 3, together with a calculation (carried out similarly to [38]) for the rotational temperature of 8 K. The majority of molecules are in the lowest rotational state N'' = 1. Application of a pump pulse train changes the spectrum dramatically by increasing the intensity of lines originated from N'' > 1. REMPI spectrum of the excited molecules, obtained with the maximum available pulse energy of 300 μ J, shows populated peaks for the rotational number as high as N'' = 19. Unfortunately, different rotational transitions in O2 overlap with one another, and it is generally difficult to have a REMPI line corresponding to a single initial state (see line assignments in Fig. 3). We use two spectral lines at 287.25 and 287.14 nm, for which the majority of ions originate from N'' = 3 and N'' = 5 rotational states, respectively. Even though the individual lines are not resolved, the relative contribution of the neighboring states to the total ion signal in both cases is estimated as <18%.

Our main results are shown in Figs. 4 and 5. With the probe wavelength set to 287.25 nm (N'' = 3) and 287.14 nm (N'' = 5), we vary δ and τ while keeping the pulse train envelope and energy (140 μ J) constant. We



FIG. 3 (color online). REMPI spectrum of cold oxygen: Experimental results (lower solid curve) and calculations (lower dashed line). Upper solid curve shows the spectrum of rotationally excited molecules (shifted up for clarity). Dashed vertical lines indicate the frequencies of transitions originated from a certain rotational state, labeled with the corresponding N'' numbers. Thick vertical arrows point at the two peaks which correspond mostly to N'' = 3 (right) and N'' = 5 (left) initial rotational states.



FIG. 4. Total excitation efficiency of oxygen molecules excited to N'' = 3 (a),(c) and N'' = 5 (b),(d) rotational state (note the difference in time scale). (a),(b) Experimental data, (c),(d) numerical calculations. Each experimental data point represents an average over 150 probe pulses. Gray scale coding: (a),(b) minimum: S = 0, maximum: S = 1 (arb. units); (c) minimum: P = 0.1, maximum: P = 0.6; (d) minimum: P = 0, maximum: P = 0.35.

record the total ionization signal for left and right circularly polarized probe, S_L and S_R , respectively. The sum of the two signals, $S = S_L + S_R$, is plotted in Fig. 4 and represents the average total efficiency of exciting the molecules to N'' = 3 and 5 as a function of δ and τ .

The experimental results are compared with a theoretical analysis of the population distribution of various rotational states of oxygen excited by the chiral train. In our model, the pulses were considered as δ kicks, and the molecular wave function was expanded in the Hund's case (*b*) basis. The nonperturbative modification of the expansion coefficients due to the interaction with every pulse was determined with the help of the numerical procedure described in [9]. Thermal averaging over initial molecular states was done to account for thermal effects. As the observables related to the measured signals, we calculated P_L (P_R)—the total population of the *N* states with positive (negative) projection M_J of the total angular momentum **J** onto the propagation direction of the chiral pulse train. The population of the $M_J = 0$ state was equally divided between P_L

and P_R . The sum of these calculated populations (*P*) for N'' = 3 and N'' = 5 is shown in Figs. 4(c) and 4(d), respectively.

Both experimental (a) and theoretical (c) plots of Fig. 4 show that for $\delta = 0$, π (nonrotating polarization) the total signal exhibits well pronounced maxima at $\tau \approx 2400$ fs and $\tau \approx 4700$ fs. As expected, these times correspond to one and two periods of "rotation" for N'' = 3, defined as $T_{N=3} = h/(E_{N=3} - E_{N=1}) = 2340$ fs. Of course, the picture of classical rotation is not applicable for such low rotational numbers, and the "period of rotation" simply means the evolution period of a rotational wave packet consisting of only two states, N'' = 1 and N'' = 3. Similar maxima are observed in Figs. 4(b) and 4(d) for about twice lower values of τ corresponding to the faster evolution of a higher angular momentum state, N'' = 5.

All panels of Fig. 4 show a characteristic "X" pattern with clear diagonal lines. Their slope defines a constant period of polarization rotation in the chiral train, $T_p = 2\pi\tau/\delta$. Diagonals with a positive slope, e.g., from



FIG. 5. Directionality of molecular rotation for N'' = 3 (a),(c) and N'' = 5 (b),(d) states (note the difference in time scale). Gray scale coding: (a) minimum: $\epsilon = -0.2$, maximum: $\epsilon = +0.2$; (b) minimum: $\epsilon = -0.4$, maximum: $\epsilon = +0.4$; (c) minimum: $\epsilon = -0.7$, maximum: $\epsilon = +0.7$; (d) minimum: $\epsilon = -0.8$, maximum: $\epsilon = +0.8$.

point ($\tau = 0$, $\delta = 0$) to point ($\tau = 2400$, $\delta = \pi$) in 4(a) and 4(c), correspond to the polarization rotating clockwise, while a negative-slope diagonal corresponds to counterclockwise polarization rotation. The population of the corresponding state is clearly higher along these diagonal lines, reflecting a higher degree of rotational excitation by a pulse train whose polarization is rotating in sync with the molecules. Note that the lines of enhanced excitation correspond to the train polarization rotating twice as slow as the molecules, e.g., $T_p = 2T_{N=3}$. The effect is reproduced in the numerical calculations shown in 4(c) and 4(d), and can be attributed to the inversion symmetry of the oxygen molecule.

Aside from the diagonals, the plots of Fig. 4 exhibit rich two-dimensional structure with notably more features visible in the case of lower (N'' = 3) rotational excitation. Our numerical analysis attributes this difference to the following two reasons. First, the spin-rotation splitting of the N'' = 3 state is more than 7 times that of N'' = 5, which makes a simple two-level wave packet model less applicable. Second, with an estimated rotational kick strength of $P \approx 7$, the lower state undergoes stronger perturbation than the upper one. Theoretical calculations with neglected spin-rotation coupling and weaker field strength result in a higher degree of similarity between the N'' = 3 and N'' = 5 cases.

Figure 5 shows the degree of rotational directionality, defined as $\epsilon = (S_L - S_R)/(S_L + S_R)$ or $\epsilon = (P_L - P_R)/(P_L + P_R)$ for the experimental observations and numerical calculations, respectively. A similar X pattern can be recognized on all panels, confirming the directionality of molecular rotation along the "resonant" diagonals. Indeed, the dark positive-slope traces correspond to $\epsilon < 0$ (clockwise rotation), whereas the bright ones with a negative slope correspond to $\epsilon > 0$ (counterclockwise rotation).

The end and center points of the X pattern in Fig. 4 (i.e., at $\delta = 0$, $\pi/2$, and π) exhibit higher signal in comparison to the intermediate values of δ . This is the result of a bidirectional rotational excitation at those points, where the pulse train is resonant with both clockwise and counterclockwise rotating molecules, and the total number of excited molecules is therefore higher. This conclusion is evident in Fig. 5, where no circular anisotropy ($\epsilon = 0$) is observed and calculated around $\delta = 0$, $\pi/2$, π .

An interesting increase in the directionality of the excited rotation is observed for low train period ($\tau = 100$ fs) and polarization rotation angle $\delta \approx \pi/2$. In this case, pulses of the chiral train are overlapping in time, forming a single pulse with gradually rotating polarization. This is almost the centrifuge field of [7,30,32,33]. In contrast to the latter, here the polarization rotation is fast at the beginning of the pulse, it then slows down to zero in the middle, and accelerates in the opposite direction towards the end of the pulse. Even though our pulse is of much lower strength and duration than that needed for spinning molecules to

high angular frequencies, its effect on low rotational state is quite evident for both N'' = 3 and N'' = 5 [Figs. 5(a) and 5(b)]. The centrifuge effect is not observed in the numerical calculations, which assume an infinitely short duration of pulses in the chiral pulse train.

In summary, we have proposed and implemented a new method of exciting unidirectional molecular rotation with polarization-shaped femtosecond laser pulses. The technique of generating a sequence of pulses with field polarization rotating from pulse to pulse by a predefined constant angle—a chiral pulse train—has been demonstrated and utilized for the rotational control of molecular oxygen. Tuning the parameters of the chiral pulse train enabled us to control both the frequency of excited molecular rotation and its directionality.

The authors would like to thank Guillaume Bussiere for the help with the REMPI setup. This work has been supported by the CFI, BCKDF, NSERC, and ISF.

- [1] B. Friedrich and D. Herschbach, Phys. Rev. Lett. **74**, 4623 (1995).
- [2] H. Stapelfeldt and T. Seideman, Rev. Mod. Phys. 75, 543 (2003).
- [3] I. S. Averbukh and R. Arvieu, Phys. Rev. Lett. 87, 163601 (2001).
- [4] F. Rosca-Pruna and M. J. J. Vrakking, Phys. Rev. Lett. 87, 153902 (2001).
- [5] J. M. Rost et al., Phys. Rev. Lett. 68, 1299 (1992).
- [6] M. J. J. Vrakking and S. Stolte, Chem. Phys. Lett. 271, 209 (1997).
- [7] J. Karczmarek et al., Phys. Rev. Lett. 82, 3420 (1999).
- [8] K. Kitano, H. Hasegawa, and Y. Ohshima, Phys. Rev. Lett. 103, 223002 (2009).
- [9] S. Fleischer et al., New J. Phys. 11, 105039 (2009).
- [10] M.Z. Hoque et al., Phys. Rev. A 84, 013409 (2011).
- [11] M. Shapiro and P. Brumer, *Principles of the Quantum Control of Molecular Processes* (Wiley-Interscience, Hoboken, NJ, 2003).
- [12] E. Gershnabel and I.S. Averbukh, Phys. Rev. Lett. 104, 153001 (2010).
- [13] H. Stapelfeldt et al., Phys. Rev. Lett. 79, 2787 (1997).
- [14] S. M. Purcell and P.F. Barker, Phys. Rev. Lett. 103, 153001 (2009).
- [15] J. Itatani et al., Phys. Rev. Lett. 94, 123902 (2005).
- [16] N. Wagner et al., Phys. Rev. A 76, 061403 (2007).
- [17] K. Tilford et al., Phys. Rev. A 69, 052705 (2004).
- [18] M. Tenner et al., J. Chem. Phys. 94, 5197 (1991).
- [19] E. W. Kuipers et al., Nature (London) 334, 420 (1988).
- [20] J. N. Greeley et al., J. Chem. Phys. 102, 4996 (1995).
- [21] R.N. Zare, Science 279, 1875 (1998).
- [22] D. Shreenivas *et al.*, J. Phys. Chem. A **114**, 5674 (2010).
- [23] J. G. Underwood, B. J. Sussman, and A. Stolow, Phys. Rev. Lett. 94, 143002 (2005).
- [24] K.F. Lee et al., Phys. Rev. Lett. 97, 173001 (2006).
- [25] D. Daems et al., Phys. Rev. Lett. 95, 063005 (2005).

- [26] L. Holmegaard *et al.*, Phys. Rev. Lett. **102**, 023001 (2009).
- [27] M. Leibscher, I.S. Averbukh, and H. Rabitz, Phys. Rev. Lett. 90, 213001 (2003).
- [28] J. P. Cryan, P. H. Bucksbaum, and R. N. Coffee, Phys. Rev. A 80, 063412 (2009).
- [29] S. Zhao et al., Chem. Phys. Lett. 506, 26 (2011).
- [30] D. M. Villeneuve et al., Phys. Rev. Lett. 85, 542 (2000).
- [31] N.V. Vitanov and B. Girard, Phys. Rev. A **69**, 033409 (2004).
- [32] L. Yuan *et al.*, Proc. Natl. Acad. Sci. U.S.A. **108**, 6872 (2011).
- [33] J. P. Cryan et al., Phys. Rev. X 1, 011002 (2011).
- [34] T. Brixner et al., Phys. Rev. Lett. 92, 208301 (2004).
- [35] F. Weise, G. Achazi, and A. Lindinger, Phys. Rev. A 82, 053827 (2010).
- [36] A. M. Weiner, Rev. Sci. Instrum. 71, 1929 (2000).
- [37] S. Zhdanovich *et al.* (to be published).
- [38] M. Mizushima and R.M. Hill, Phys. Rev. 93, 745 (1954).