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Adaptive control of molecular alignment

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We demonstrate control on nonadiabatic molecular alignment by using a spectrally phase-shaped laser pulse. An evolutionary algorithm in a closed feedback loop has been used in order to find pulse shapes that maximize a given effect. In particular, this scheme has been applied to the optimization of total alignment, and to the control of the temporal structure of the alignment transient within a revival. Asymmetric temporal pulse shapes have been found to be very effective for the latter and have been studied separately in a single-parameter control scheme. Our experimental results are supported by numerical simulations.

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Molecules that are irradiated by a laser pulse of a duration much shorter than the rotational period undergo transient alignment immediately after the laser pulse. The subsequent rotational dynamics produce alignment recurrences after multiples and fractional multiples of the rotational period. This nonadiabatic alignment of molecules using ultrashort laser pulses has become a powerful tool to prepare spatially aligned samples of molecules in the gas phase [1]. Related experimental [2–6] and theoretical studies [7–9] on molecular alignment have focussed on the effects of a single Fourier-transform-limited (FTL) laser pulse and two or more pulses [10–16] with a temporal separation on the time scale of the molecular revival structures. More recently, efforts have been directed to control nonadiabatic molecular alignment by using pulse-shaping techniques [12,17,18]. In particular, Renard *et al.* have employed specific phase masks to create pulses that control the relative contribution of even and odd rotational states within the rotational wave packet [12,18].

In the present work we perform a more general exploration of pulse shaping to investigate how much control it is possible to attain in molecular alignment and on the dynamics of the rotational wave packets produced by a phase-shaped laser pulse. The large number of possibilities that open up when applying an arbitrary phase function can be conveniently explored by a closed feedback loop procedure in combination with evolutionary algorithms [19,20]. In the present work, the defined targets are the optimization of the total degree of alignment, and the control on the temporal structure of molecular alignment within a revival. We show that asymmetric temporal pulse shapes exert control on the angular distribution of the rotational wave packet in a diatomic molecule. We confirm this scheme in a single-parameter control experiment using spectral phase masks that induce third order dispersion (TOD) in the spectrum of the laser pulse.

The phenomenon of dynamical alignment induced by a short nonresonant laser pulse originates from Raman-type transitions creating coherent rotational wave packets. For homonuclear diatomics and linearly polarized electric fields, an effective Hamiltonian can be, apart from an angle-independent term, written as [4,21]

$$H_{\mathrm{eff}} = B\mathbf{J}^2 - \frac{1}{4}|\varepsilon(t)|^2 \Delta\alpha \cos^2\theta, \tag{1}$$

where B and $\mathbf{J}$ are the rotational constant and the angular momentum of the molecule, respectively, $\varepsilon(t)$ is the envelope function of the electric field, $\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp}$ is the difference between the parallel and perpendicular components of the polarizability tensor of the molecule, and θ is the angle between the molecular axis and the polarization direction of the electric field.

Due to the symmetry of the Hamiltonian, an initially pure rotational eigenstate $|\psi_{J_0,M_0}(t=0)\rangle = |J_0, M_0\rangle$ can only undergo transitions with $\Delta M = 0$ and $\Delta J = \pm 2$. If the field intensity is high enough this leads to rotational ladder climbing. After the interaction with the laser pulse the resulting wave packet can be written in the form

$$|\psi_{J_0,M_0}(t)\rangle = \sum_{J \geq |M_0|} c_J^{J_0,M_0} e^{-i(E_J t/\hbar)} |J, M_0\rangle, \tag{2}$$

where $E_J = BJ(J+1)$ is the rotational energy and the coefficients $c_J^{J_0,M_0}$ depend on the details of the laser interaction. Due to the selection rules only Js with $J \geq |M_0|$ and even valued $J - J_0$ contribute to the wave packet. For such a wave packet, the observable $\langle \cos^2\theta \rangle_{J_0,M_0}(t)$ takes the form of beat structures oscillating rapidly with frequencies $\omega_J = (E_{J+2} - E_J)/\hbar$ [12].

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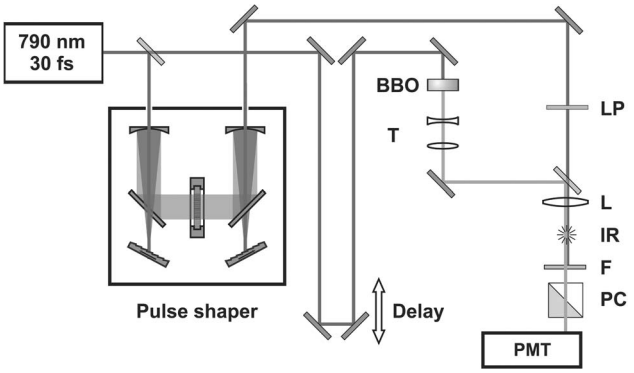

FIG. 1. Sketch of the experimental setup. BBO, second harmonic generation crystal; T, telescope (1:2) to increase the beam diameter; LP, $\lambda/2$ plate, rotates the pump polarization vector by 45°; L, focussing lens; IR, interaction region; F, filter to eliminate the pump laser; PC, polarization cube; PMT, photomultiplier.

For a gas sample that is initially in thermal equilibrium, a convenient measure of alignment is $\langle\langle\cos^2\theta\rangle\rangle$, where the double angular bracketing indicates ensemble averaging. The time dependence of $\langle\langle\cos^2\theta\rangle\rangle(t)$ differs structurally from that of a single state due to the incoherent addition of the initial rotational states. The fast oscillations cancel out leaving nonvanishing alignment only at times of the so-called revivals occurring at integer (and fractional) multiples of the rotational period $T_r=\pi\hbar/B$ well known from rotational coherence spectroscopy (as reviewed in, e.g., [22]). The goal of the investigation presented in this paper is to influence the temporal shape of these transients using shaped laser pulses.

A numerical calculation has been performed to solve the time-dependent Schrödinger equation in the basis of field-free stationary rotational states $|J,M\rangle$ of the molecule. Only the matrix elements $\langle J,M|\cos^2\theta|J,M\rangle$ and $\langle J,M|\cos^2\theta|J\pm2,M\rangle$ are nonzero. For a given initial wave function $|\psi_{J_0,M_0}(t=0)\rangle$, M_0 remains fixed and the final wave function after the interaction consists of a superposition of either only odd or even J states. With increasing laser intensity, more J states become significantly populated. Finite temperature is considered by a thermal ensemble of initial wave functions weighted by the Boltzmann factor and the multiplicity due to nuclear spin statistics.

The experimental setup is depicted in Fig. 1. The alignment is induced by a femtosecond laser pulse centered at 790 nm, with a full width at half maximum (FWHM) of 30 fs. The peak intensity was estimated to be $I\approx5\times10^{13}$ W/cm^2 by taking the measured pump beam focus into account. The laser pulse passes through a pulse shaper [23,24] and is then focussed with a $f=10$ cm lens into the interaction region. Alignment transients are observed on N_2 and O_2 contained in air at room temperature. For measuring the created alignment transients, a technique sensitive to the instantaneous birefringence of the media is used [5,25]. For that purpose, a delayed 395 nm laser pulse, obtained by second harmonic generation in a beta-barium-borate (BBO) crystal, probes the interaction region. The polarization vector of the pump pulse was set at an angle of 45° with respect to that of the probe pulse by rotating the pump pulse polarization vector with the help of a $\lambda/2$ plate. The laser-induced birefringence in the molecular ensemble changes the polarization state of the probe laser by introducing some ellipticity after the interaction region. The beam is filtered through an analyzing polarizer cube and the new polarization component is detected by a photomultiplier.

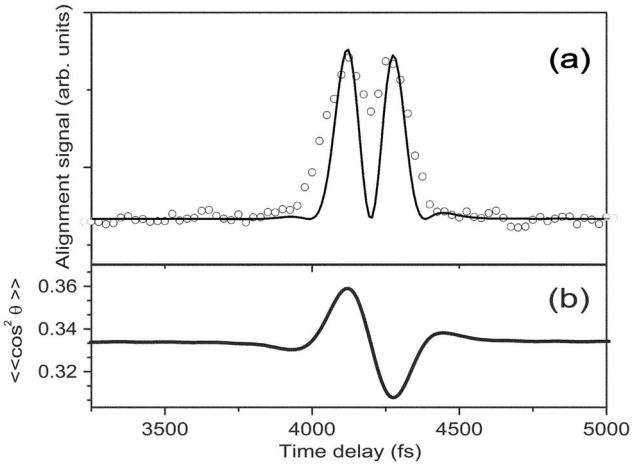

FIG. 2. Alignment transient of the first half revival in N_2 at room temperature for a FTL pulse. (a) Experimental (circles) and calculated (solid line) homodyned alignment signal. (b) Calculated values of $\langle\langle\cos^2\theta\rangle\rangle$ for $T=300$ K and $I\approx5\times10^{13}$ W/cm^2.

Optimization of the shape of the pump pulses by application of phase masks in the Fourier plane has been performed by an GENITOR-type evolutionary algorithm [26] in a closed feedback loop. In each evolution step one or two individuals of a population of $N=50$ were selected with a probability which increases exponentially with their fitness rank. From those individuals, a child is produced according to one of five different operators: uniform crossover, average, mutation, and two different creep operators. The choice of operator is random in the beginning, but successful operators are rewarded with higher probabilities during the course of the evolution.

Since in terms of overall stability of the experiment it is desirable to have a fast convergence, we have reduced the parameter space by using only the first six terms of a Taylor expansion to parametrize the phase. Test runs confirmed that this gave much better results in the limited time available for one optimization than a full parametrization using 128 genes representing all of the available pixels of the phase mask.

The optimization procedure was applied on the region of the first half-revival of N_2, appearing at a time delay of $\tau\approx T_r/2\approx4.2$ ps. This region has the advantage that there is no overlap with O_2 recurrences. Figure 2 shows the result obtained for a FTL pulse. The rotational half revival structure consists of two peaks, the first of which, appearing at an earlier delay, corresponds to the situation of alignment, where the internuclear axes of the N_2 molecules are preferentially aligned parallel to the incident laser polarization. The second peak corresponds to the situation of antialignment (also called planar delocalization), where the molecules align preferentially in the plane perpendicular to the polarization vector of the laser. In the figure, both peaks appear with the same sign because homodyned detection [5] was employed.

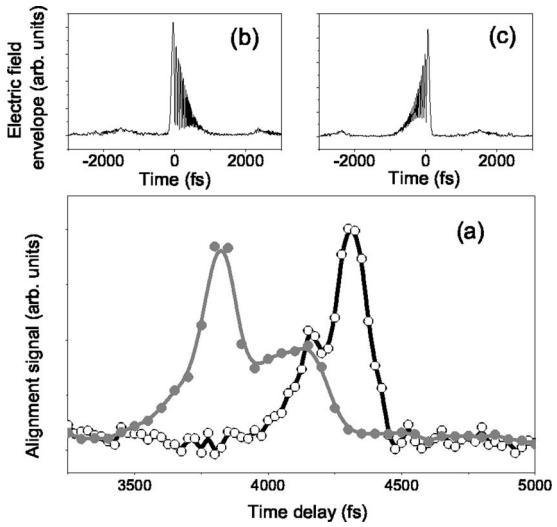

FIG. 3. Closed-loop evolutionary control of the temporal structure of alignment revivals. (a) Alignment transients for the first half-revival of N_2 corresponding to the best individuals of two evolutionary runs. Solid circles: optimization of alignment versus antialignment. Open circles: optimization of antialignment versus alignment. The curves are intended as visual guides. (b) Envelope of the electric field amplitude of a representative good individual for maximization of alignment versus antialignment. (c) Same as (b) for maximization of antialignment. See text for details.

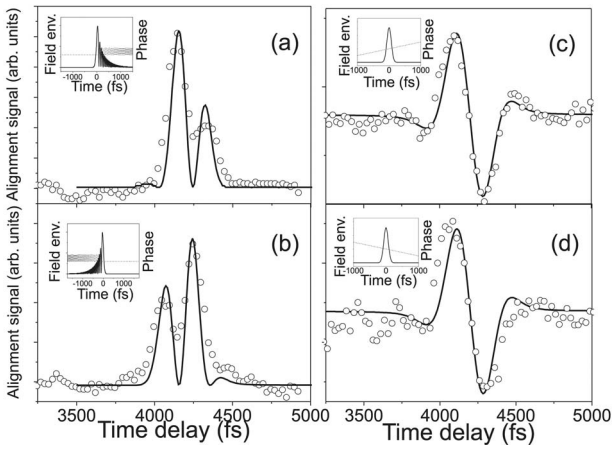

FIG. 4. (a) and (b) Control of the relative magnitude of alignment and antialignment in the first half-revival of N_2 by applying pulses with TOD. (a) Enhancement of alignment versus antialignment by application of a pulse with positive TOD. (b) Enhancement of antialignment versus alignment by application of a pulse with negative TOD. (c) and (d) Heterodyned measurements of the effect of applying pulses with linear chirp. The structure of the first half-revival of N_2 remains unchanged. The dots are experimental results; the lines correspond to numerical simulations. The insets show the amplitude and phase of the electric field envelope in the time domain.

The first fitness criterium applied was the search for the optimization of the total alignment signal. The pulses found by the algorithm which produced strongest alignment were very similar in temporal shape to a FTL pulse and the measured fitness was accordingly comparable. This result is in accordance with experimental evidence found by Renard *et al.* [12].

Most of the subsequent work was then devoted to study control on the temporal structure of the revival. The fitness function was chosen to be the ratio between the intensity of the peak corresponding to alignment and that corresponding to antialignment. After a few generations, the evolutionary algorithm found individuals whose fitness function was significantly higher than any of the individuals in the initial population. This is demonstrated in Fig. 3, which shows the half-revival transients produced by the best individuals of two runs which maximized alignment versus antialignment and vice versa. This constitutes proof of the success of the evolutionary procedure applied to this particular problem.

Often there is no straightforward way of shedding light onto the relevant physical mechanisms given the optimal pulse forms found by an evolutionary algorithm. In this case, the analysis of the phase masks in the frequency domain that were applied to the best individuals did not produce a simple picture. However, by considering the temporal structure of the best pulses we found distinct recurrent features. The top section of Fig. 3 shows temporal pulse shapes representative of the best individuals of each optimization. The type of pulse shape represented corresponds to a large class of individuals with high fitness. The pulse form of some of the best individuals was verified experimentally by frequency resolved optical gating techniques [27]. As can be clearly seen, pulses that optimized alignment versus antialignment presented a steep leading edge and a slowly decaying trailing edge while the inverse was observed for the pulses that optimized antialignment. It seems then that the key feature in the optimization are these rather general properties of the temporal field envelope rather than more subtle details of the applied phase function.

The consistent asymmetry of the temporal shapes found by the algorithm led us to search for single-parameter control schemes that would simplify the description of the physical mechanism. The lowest order coefficient in a Taylor series that can produce asymmetric pulse shapes is the one that corresponds to TOD. Therefore, we performed a systematic study of its effect on the revival structure. The TOD Taylor expansion coefficient was scanned from $-120\,000$ fs^3 to $+120\,000$ fs^3 in steps of $12\,000$ fs^3. The two left panels of Fig. 4 show the results obtained with the extreme values of the TOD parameter. Intermediate values yielded intermediate results. The same type of temporal shape asymmetry in the pulse produces the same effect on the alignment transient as was found via the evolutionary algorithm. For comparison, linear chirp with a magnitude of ± 600 fs^2 was also applied. As shown in the right panels of the figure, no influence could be exerted on the relative intensities of the alignment and antialignment peaks in this case. This was expected from the Hamiltonian, Eq. (1), which is only sensitive to the temporal amplitude envelope of the field rather than its phase.

For these panels, the detection method used was heterodyned [5], and thus sensitive to the sign of the alignment. For both quadratic and cubic phase masks, numerical simulations were performed as described above and the results are shown as solid lines in the figure. The agreement with experimental data supports the experimental evidence that control on the

asymmetry of the temporal shape of the laser pulse provides substantial control of the relative strength of alignment and antialignment. More numerical work is in progress to gain further insight into the physical mechanism that maps the asymmetry of laser pulses onto the enhancement of alignment versus antialignment or vice versa.

In summary, it has been shown that the dynamics of nonadiabatic laser-induced molecular alignment can be modified by intervening in the temporal structure of the laser pulses. Optimization methods have been successful in guiding the search for pulse shapes that optimize desired effects. In particular it was possible to control the relative intensities of the alignment and antialignment peaks in the temporal structure of the half-revival of N_2 using asymmetric temporal pulse shapes. In order to understand the mechanism for control it will be important to investigate further the interplay between coherent and incoherent effects present in the laser-induced alignment of a thermal molecular ensemble which is connected to the question of controllability at low temperatures. Preliminary simulations have shown that the TOD control scheme gives significant control also for temperatures as low as 50 K. These topics will be explored in a future publication.

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