Probing nonadiabatic molecular alignment by spectral modulation

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Abstract: We investigated molecular alignment wakes of femtosecond laser pulses. Evolution of nonadiabatic molecular alignment in nitrogen gas has been measured via its nonlinear interaction effects with a variably delayed probe pulse. The induced rotational wave packet was mapped as a function of the angular difference between polarization directions of femtosecond pump and probe pulses as well as their relative delay and the plot of the variations of the rotational wave packet, i.e. “quantum carpet”, was found to be in good agreement with the calculated angular and temporal dependencies of molecular alignment parameter.

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References and links

1. Introduction

When exposed to an intense and short femtosecond pulse, atomic and molecular media show highly nonlinear dynamics leading to phenomena such as high harmonic generation from filaments [1], long-range filament propagation [2], ultrashort pulse shaping and white-light generation [3, 4], as well as molecular alignment [5]. The interaction of a strong laser pulse with a molecule creates an induced dipole moment due to the anisotropic polarizability of the molecule, and the molecule tends to align with its most polarizable axis along the laser polarization direction [6]. If the laser pulse is short, i.e. its duration is less than the characteristic molecular rotational time, the molecules cannot be adjusted adiabatically by the laser pulse, so this process is called “non-adiabatic (field-free) alignment” [7–9]. In the nonadiabatic alignment, the short laser pulse creates in each molecule a rotational wave packet, coherent superposition of the rotational states that will rephase and dephase in time after the laser pulse has ended. After the alignment, the absence of the aligning laser field prevents distortion of the molecular alignment caused by the field, therefore nonadiabatic alignment has this advantage in comparison with adiabatic alignment in observing molecular dynamics [10–12].

The nonlinear polarization exerted by a pump pulse yields an intensity-dependent refractive index and a transient birefringence as a result of the pulse interaction with the molecular gas. Then a probe pulse propagates in a medium with properties that depend on the delay in the wake of the pump pulse. For certain conditions, the intense probe pulse can experience self-focusing and spatially collapse due to the dynamic Kerr effect. This collapse however stops when the intensity becomes high enough to generate free electrons and nonlinear losses tending to defocus the beam resulting in filamentary propagation [13]. The spatial and temporal characteristics of the aligned molecules affect filamentation and white light generation [14], so the latter process can be used as a probe to monitor the dynamics of molecular alignment.

The nonadiabatic molecular alignment was studied with filamentation and white-light generation in recent years [5,15–20]. It was shown that pre-aligned molecular gases can change the starting position [18] or increase the propagation distance of a filament [16]. The possibilities to control the length of two co-propagating filaments by creating molecular alignment [5] or a secondary filament emission, such as THz radiation [21,22] and
supercontinuum generation [23] were also shown. In addition, the effect of molecular alignment on pulse compression [3] and its potential applications in attosecond physics were demonstrated [24,25]. The effects of the quantum interference in high order harmonic generation in impulsively aligned CO₂ molecules were studied in Refs [26,27]. However, the complete angular evolution of the rotational wave packet for pump-probe experiments with different polarizations was not measured.

In this study, we have used transmission spectral modulation of a probe pulse to determine molecular dynamics of non-ionized impulsively aligned medium. The variable in time degree of molecular alignment affects the bandwidth and magnitude of spectral components of the probe pulse, resulting in variations of the total transmitted power. Then, by changing the angle between polarizations of the pump pulse and the filament-producing probe pulse and performing measurements for a range of pump-probe delays around rotational revivals, we obtained a map of the rotational wave packet as a function of the polarization mismatch and delay between the pump and probe pulses, which is also known as a “quantum carpet” [28,29]. The experimental results from mapping rotational wave packets are compared with quantum mechanically calculated angular and time dependencies of the molecular alignment parameter.

2. Experimental procedures

Our experiments were done with a Ti:sapphire amplified laser system, which has a pulse duration of ~50 fs, central wavelength of 800 nm, and an output energy of 1 mJ per pulse at a 1 kHz repetition rate. The output radiation is split into two parts by a beam splitter (BS-1) to obtain the pump and probe pulses as shown in Fig. 1. The delay time of the probe pulse with respect to the pump pulse was precisely adjusted using a variable time delay with a translational stage controlled by a stepping motor (GTS150, ESP300, Newport). To adjust the polarization direction and intensity of the pump beam we used a combination of a half wave plate and a polarizer precisely controlled by two computer Picomotor rotary stages (New Focus, Model 8701). The two pulses with a relative delay were recombined with a beam splitter BS-2, and the pump pulse polarization could be rotated with respect to that of the probe pulse by an arbitrary angle $\alpha$.

![Fig. 1. The schematic of the experimental setup. BS: beam-splitters, TS: translational stage, WP: wave plate, P: polarizer, M: flat mirrors, FL: focusing lens, PM: power meter.](image)

The recombined beams were then focused using a lens FL-1 with a focal length of $f = 60$ cm into a sealed gas cell of 85 cm length. The cell was filled with 99.9995% purity N₂ gas (Matheson TRIGAS) to a maximum pressure of 4 bar. After evacuating it down to $2 \times 10^{-3}$ mbar the pump pulse was adjusted to have an intensity ($=5 \times 10^{12}$ W/cm²), which was high enough for aligning purposes, but too low to modify the spectrum. The intensity of the probe pulse at the focus was set to $=10^{13}$ W/cm² (we note that filaments form due to the dynamic
balance of the Kerr self-focusing and plasma defocusing at somewhat higher intensity values
[30]) to observe and measure the alignment produced by the probe pulse using nonlinear
spectral modulation as an indicator. By blocking the probe pulse, we checked that no spectral
modification was produced with the pump pulse only. At the exit of the gas cell, the probe
pulse signals and durations of the pulses were measured by reflecting a small portion of the
beams with a beam splitter (BS-3) positioned after the cell. The transmitted light was
collimated by FL-2, attenuated to desired level by a filter, and the power measurement of the
probe pulse variations were performed by using a photodiode power meter (Ophir NOVA II
with PD300-UV head) with a spectral range within 200-1100 nm. In the spectral
measurements were performed with an Ocean Optics USB-2000 spectrometer. The pulse
duration measurements were taken with a correlator Grenouille (8-20, Swamp Optics). We
automated the experiments using National Instruments (NI) DAQ PCI-MIO-16E-4 card, NI
BNC 2090 box and a custom NI LabVIEW program that controlled the entire experiment and
data collection.

3. Theory

3.1 Nonadiabatic molecular alignment

We consider a linear molecule subjected to a linearly polarized laser field with the Gaussian
distribution \( \varepsilon(r,t) = g(t)e_y(r)\cos(\omega t) \), where \( e_y(r) \) is the local electric field amplitude, \( \omega \) is
the laser central frequency, and \( g(t) = \exp\left[\left(-2\ln 2\right)t^2/\tau^2\right] \). \( \tau \) is the pulse duration. Since
the scale of the spatial changes of the electric field is much larger than the atomic scale, to
find local alignment parameters we can assume the field amplitude to be constant, thus we
disregard the spatial dependence on \( r \) in this part and restore it in the final expressions.
Therefore, the time-dependent Schrödinger equation describing a molecule in an intense laser
field can be written based on the rigid rotor model [31,32] as

\[
\frac{i\hbar}{\partial t} \Phi_{JM}(t) = \left( H^{(0)}_R + V_I(t) \right) \Phi_{JM}(t),
\]

where \( H^{(0)}_R = B\hat{J}^2 \) is the field-free rotational Hamiltonian of the molecule with \( B \) and \( \hat{J} \)
being the rotational constant and the angular momentum operator, respectively;
\( V_I(t) = -\frac{1}{2}\left( \Delta \alpha \cos^2 \theta + \alpha_\perp \right) \varepsilon^2(t) \) is the interaction term of a linear symmetric top
molecule subjected to linearly polarized laser field \( \varepsilon(t) \) of the field of the pump pulse
[31,33]; \( \Delta \alpha \) is the difference between parallel \( \alpha_\parallel \) and perpendicular \( \alpha_\perp \) polarizability
components with respect to the molecular axis, and \( \theta \) is the angle between the molecular axis
and the pump laser field polarization.

The rotational wave function \( \Phi(t) \) can be expanded in a sum of free-field rotor
eigenfunctions \( |JM| \) with eigenenergies \( E_J = BJ(J+1) \), where \( J \) is an integer of the
orbital momentum quantum number, and for each \( J \) the projection quantum number \( M \)
takes the values \( -J, -(J-1), ..., 0, ..., (J-1), J \). Then the evolution of the initial state,
\( |\Phi_{JM_\perp}(t)\rangle \), created by the pump pulse is described by an expansion in the rotational wave
packet states [9,34,35]:

\[
|\Phi_{JM_\perp}(t)\rangle = \sum_M d_{JM_\perp}^{JM_\parallel}(t) \exp\left(-i\frac{E_J t}{\hbar}\right)|JM_\parallel\rangle,
\]

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where the expansion coefficients $d_{JM}^{J_0M_0}(t)$ are determined by solving the set of differential equations [8] stemming from the time-dependent Schrödinger Eq. (1).

The degree of alignment evolving from a given initial state $|J_0M_0\rangle$ is characterized by

$$\langle \cos^2 \theta \rangle_{J_0M_0}(t) = \langle \Phi_{J_0M_0}(t) | \cos^2 \theta | \Phi_{J_0M_0}(t) \rangle.$$  

Before the interaction, the gas ensemble is assumed to be in thermal equilibrium with Boltzmann distribution at temperature $T$. In the quantum-mechanical approach, the ensemble is described by a statistical mixture of states $|J_0M_0\rangle$ with different angular momenta, where again $J_0 = 0, 1, 2, \ldots$ and $M = -J_0, -(J_0 - 1), \ldots, 0, \ldots (J_0 - 1), J_0$. The probabilities of $|J_0M_0\rangle$ states follow Boltzmann distribution $P_{J_0} \sim (2J_0 + 1) \exp(-E_{J_0}/kT)$, where $E_{J_0}$ is the rotational energy of $|J_0M_0\rangle$ state and $k$ is the Boltzmann constant. The $(2J_0 + 1)$ term accounts for the degeneracy within a given $J_0$ state.

For a complete description, the influence of nuclear spin of atoms constituting the molecule must be taken into account. Consequently, an additional factor $g_{J_0}$ originating from the nuclear spin statistics appears in the Boltzmann distribution:

$$P_{J_0} \sim g_{J_0} (2J_0 + 1) \exp(-E_{J_0}/kT).$$

Finally, the degree of alignment of an ensemble at temperature $T$ can be found by averaging the different states over the Boltzmann distribution including nuclear spin statistics

$$\langle \langle \cos^2 \theta \rangle \rangle(t) = \frac{\sum_{J_0} \sum_{M_0=-J_0}^{J_0} g_{J_0} \langle \cos^2 \theta \rangle_{J_0M_0}(t) \exp(-BJ_0(J_0 + 1)/kT)}{\sum_{J_0} \sum_{M_0=-J_0}^{J_0} g_{J_0} \exp(-BJ_0(J_0 + 1)/kT)},$$

where $\langle \langle \cos^2 \theta \rangle_{J_0M_0}(t)$ is the alignment degree for a single individual state in the vicinity of a spatial location $r$. For the nitrogen molecule, $g_{J_0} = 6$ for even $J$'s and $g_{J_0} = 3$ for odd $J$'s [36,37]. The ratio of even to odd states is therefore 2:1. It is important to note that the alignment degree is sensitive to molecular properties, i.e., the rotational constant $B$, statistical weight factors $g_{J_0}$, the ensemble temperature $T$ and the “kick” parameter, which is proportional to $\Delta \alpha$ (as well as to the laser flux) [38].

### 3.2 Description of an alignment-induced change of the refractive index

When molecules with anisotropic polarizability experience the aligning (pump) pulse in a non-adiabatic alignment regime, the refractive index changes both spatially and temporally. The nonadiabatic molecular alignment induces a periodic modulation of the refractive index $\Delta n_t(r,t)$ of a gas. For the probe pulse with the polarization direction of the aligning pulse [39]

$$\Delta n_t(r,t) = \frac{2\pi N}{n_0} \Delta \alpha \left( \langle \langle \cos^2 \theta \rangle \rangle(r,t) - \frac{1}{3} \right),$$

where $\langle \langle \cos^2 \theta \rangle \rangle(r,t)$ is the thermally averaged alignment expectation value given by Eq. (4), $N$ is the molecular density, and $n_0$ is the linear refractive index. Here we explicitly
introduced the spatial dependence, which follows the intensity distribution of the pump beam and thus creates an additional lensing effect for the probe beam due to the spatially inhomogeneous molecular alignment. The change in the refractive index for the probe polarization perpendicular to the pump field polarization is described by [40,41]:

$$\Delta n_\perp(r,t) = \frac{1}{2} \Delta n_i(r,t) = \frac{\pi N}{n_0} \Delta \alpha \left( \left\langle \cos^2 \theta \right\rangle(r,t) - \frac{1}{3} \right),$$

(6)

The resulting birefringence can be characterized by the difference [5,42,43]

$$\Delta n(r,t) = \Delta n_i(r,t) - \Delta n_\perp(r,t) = \frac{3\pi N}{n_0} \Delta \alpha \left( \left\langle \cos^2 \theta \right\rangle(r,t) - \frac{1}{3} \right),$$

(7)

i.e., the change of the refractive index is proportional to the deviation of the alignment degree from the isotropic one, which equals to 1/3. The real part of the expressions of Eqs. (5-7) determines the changes of the speed of light and the imaginary part determines the absorption of light. We note that polarizabilities can be modified when the field becomes sufficiently strong, in particular, absorption can include also the contribution from multiphoton processes. Since $n_i - 1 = \alpha N / 2$, where $n_0 = n'_0 + i n''_0$, $\alpha$ is the average polarizability of the gas, and $n'_0 >> n''_0$, it follows from Eq. (7), both changes of the real and imaginary parts of the refractive index are proportional to the alignment factor,

$$\Delta n(r,t) = (6\pi) \frac{\left( n_i - 1 \right)}{n_0} \left( \Delta \alpha \right) \left( \left\langle \cos^2 \theta \right\rangle(r,t) - \frac{1}{3} \right),$$

(8)

and can be used for the alignment monitoring.

4. Results and discussion

4.1 Molecular alignment observation with parallel polarizations of pump and probe pulses

Figure 2(a) shows the experimental molecular alignment results in nitrogen gas at 300K compared to the calculated alignment-induced change of the refractive index, proportional to $\left\langle \left\langle \cos^2 \theta \right\rangle \right\rangle - 1/3$. The alignment was monitored by measuring the total transmitted power, attenuated to a desired level. When the polarization of the probe pulse is oriented parallel with the preferential direction of molecular axes (parallel case), an increase of the transmission was observed. When the probe pulse field polarization is perpendicular the preferential direction of molecular axes (perpendicular case), a decrease of the transmission is produced. This agrees with the assumption that $| \text{Im}(\alpha_\|) | > | \text{Im}(\alpha_\perp) |$; another possible explanation could be a redistribution of the intensity in the cross section of the beam, which is however unlikely, because the aperture of the power meter was significantly larger than the diameter of the beam. The observed enhancement of the transmitted power corresponds to an increase of the alignment parameter $\left\langle \left\langle \cos^2 \theta \right\rangle \right\rangle - 1/3$ and vice versa, which is also in agreement with the observed variations of the spectrum in Fig. 2(b).

The effect of the pulse compression with filament formation was discussed in several papers [4,44,45], where this effect was mainly attributed to the reshaping of the pulse in the process of self-focusing and subsequent filament propagation. Effects of pulse reshaping due to non-adiabatic (impulsive) molecular alignment were investigated in [17,19] and was also simulated with a time-dependent nonlinear envelope equation [46]. These simulations have shown that the strongest compression is expected at the steep slope of the temporal dependence of the refractive index due to alignment, which however is not corroborated by
our data. Figure 2(c) shows the changes of the pulse duration of the probe pulse after it propagated through the gas with the probe-pump delay. The pulse duration anti-correlates with the variations of the alignment parameter (and those of the refractive index according to Eqs. (5-7), which means that the probe pulse after the interaction with molecules subjected to the pump pulse is the shortest for aligned molecules and the longest for anti-aligned molecules as seen in Fig. 2(c).

![Image](https://example.com/image.png)

**Fig. 2.** (a) Temporal evolution of the experimentally measured probe pump power (red circles) compared to theoretically calculated nonlinear refractive index (solid black line) (b) measured spectrum of the transmitted probe beam modulated by alignment revivals, and (c) the experimentally measured pulse duration (red circles) with variations induced by molecular alignment for different relative delays between the pump and probe pulses.

The measured relative peak-to-peak variations of the transmission of the probe beam due to alignment revival were about 0.02. In additional series of experiments we found that the transmission of the probe beam through the gas cell was about 0.953 for $I_{\text{probe}} = 10^{11} \text{W/cm}^2$ and about 0.989 for $I_{\text{probe}} = 5 \times 10^{11} \text{W/cm}^2$, which shows a significant contribution of the nonlinear absorption processes. Assuming that the main part of the nonlinear absorption takes place on the length of two Rayleigh ranges in the focal region, we obtain an estimate for the imaginary part of the refractive coefficient $n'' \sim 1.5 \times 10^{-7} \text{cm}^{-1}$. Correspondingly, the experimentally determined peak-to-peak variations due to alignment are $\Delta n'' \sim 3 \times 10^{-8} \text{cm}^{-1}$. For linear polarizabilities $|\Delta \alpha/\alpha| \sim 0.039$ and at $I_{\text{pump}} = 5 \times 10^{12} \text{W/cm}^2$ and $\tau = 140 \text{fs}$, $(\langle \cos^2 \theta \rangle)^{-1/3} \sim 0.045$, therefore Eq. (8) provides an estimate for the relative variations of the transmission losses $|\text{Im}(\Delta n)/\text{Im}(n_0 - 1)| \sim 0.03$, which gives an order of magnitude smaller transmission modulation than the experimentally observed one. This again can point out that the nonlinear contributions to polarizabilities play a major role.

We note that at zero delay of the pump and probe beams we observed a bright white light with a spectrum extending down to ~500nm, which corresponds to intensity about 4 times
higher, \( I = 4 \times 10^{13} \text{W/cm}^2 \) than the intensity of the probe beam used in our experiments for monitoring revivals. An estimate shows that at such an intensity the refractive index change due to alignment \( \Delta n_{\text{align}} = \Delta n(r, I) \) produced by the pump beam becomes comparable to the refractive index change caused by the optical Kerr effect, \( \Delta n_{\text{Kerr}} = n_2 I_{\text{probe}} \). With \( n_2(N_2) = 2.3 \times 10^{-19} \text{cm}^2/\text{W} \) and \( I_{\text{probe}} = 4 \times 10^{13} \text{W/cm}^2 \), we obtain \( \Delta n_{\text{Kerr}} = 3.7 \times 10^{-5} \) for a typical gas pressure of 4 bar. The amplitude of the refractive index variations due to alignment \( \Delta n \) estimated with Eq. (7) exceeds this \( \Delta n_{\text{Kerr}} \) value for a pump pulse with intensity \( I_{\text{pump}} = 2 \times 10^{13} \text{W/cm}^2 \) (pulse duration \( \tau = 140 \text{fs} \) is assumed), which shows that a strong spectral modulation of white-light can be expected at such and higher intensities. The additional contribution to the refractive index caused by the alignment varies across the laser beam, following intensity variations, and thus changes the self-focusing length. Consequently, the dynamics of the rotational wave packet changes the filament formation and should result in modulation of the white-light generation. Indeed, in [47,48] at intensities \( I_{\text{probe}} = (1.5 - 3.7) \times 10^{13} \text{W/cm}^2 \) of the probe beam the variations of the white-light generation as a result of alignment revivals in CO2 at pressure ~2 bar were observed.

For interpretation of the revival structure, we will consider the total wave function of the linear molecule, which according to the Born-Oppenheimer approximation can be factorized \( \Psi_{\text{tot}} = \psi_{el} \times \psi_{\text{vib}} \times \psi_{\text{rot}} \times \psi_{\text{ns}} \), as a product of the electronic wave function \( \psi_{el} \), the vibrational wave function \( \psi_{\text{vib}} \), the rotational wave function \( \psi_{\text{rot}} \), and the nuclear spin wave function \( \psi_{\text{ns}} \). According to the nuclear spin statistics of \( ^{14}\text{N}_2 \), for this molecule the total wave function \( \Psi_{\text{tot}} \) is symmetric [49]. The electronic wave function of \( ^{14}\text{N} \), \( \psi_{el}(\sum \phi_j) \), and the vibrational wave function, \( \psi_{\text{vib}} \) corresponding to the ground state are also both symmetric [50]. Therefore, to understand \( \psi_{\text{rot}} \) behavior, we should consider symmetric and antisymmetric forms of nuclear spin wave function \( \psi_{\text{ns}} \) of the nitrogen molecule. For \( \Psi_{\text{tot}} \) to be symmetric both \( \psi_{\text{rot}} \) and \( \psi_{\text{ns}} \) must be symmetric or antisymmetric. The nuclear spin of \( ^{14}\text{N} \) is \( I = 1 \) and the total nuclear spin of the molecule can take only values \( I_{\text{tot}} = 0, 1, 2 \), and consequently \( \text{N}_2 \) has even \( (I_{\text{tot}} = 0, 2) \) and odd \( (I_{\text{tot}} = 1) \) values. For a state with total nuclear spin \( I_{\text{tot}} \) the degeneracy is \( 2 I_{\text{tot}} + 1 \), and then the statistical weights of even-\( \text{N}_2 \) and odd-\( \text{N}_2 \) are 6 and 3, respectively. Thus, the relative ratio of even-\( \text{N}_2 \) versus odd-\( \text{N}_2 \) is 2:1 [51]. Due to this ratio for even/odd states, the two opposed quarter revival signals do not completely cancel each other, however, the corresponding signals have reduced amplitudes in comparison to the signals at the full and half revival times, as is obtained in the experiment and quantum mechanical calculations as in Fig. 2(a).

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Fourier transform spectrum of the signal provides information regarding the populations of different \( J \) states in the rotational wavepacket. In Fig. 3 we show the corresponding frequency spectrum of the time-dependent molecular alignment signal obtained by the Fourier transform. The spectrum reveals two sequences \( (6, 14, 22, 30, 38, \ldots) Bc \) and \( (10, 18, 26, 34, 42, \ldots) Bc \). Recall that the only nonzero matrix elements of \( \langle \cos^2 \theta \rangle \) are \( \Delta J = 0, \pm 2 \) and allowed Raman transitions satisfy the selection rule \( \Delta J = \pm 2 \). Because the nuclear spin of the nitrogen nucleus is 1, both even and odd rotational states are permitted for the nitrogen molecule. Then, the sequence of spectral peaks can be calculated as \( (E_{J+2} - E_J)/2\pi = (4J + 6)Bc \) as 6, 14, 22, 30, 38, \ldots for even \( J \)’s and 10, 18, 26, 34, 42, \ldots for odd \( J \)’s. The observed larger amplitudes of the peaks seen in the frequency spectrum for the even \( J \)-states compared to the odd \( J \)-states qualitatively corresponds to the ratio 2:1.
between the populations of the even and odd $J$-states following from the nuclear spin statistics [51–53].

Fig. 3. Frequency spectrum of the time-dependent alignment signal shown in Fig. 2(a). The number on each spectral peak shows the frequency in terms of $4J + 6$ corresponding to the allowed Raman transitions given by the series (6, 14, 22, 30, 38, 46, \ldots)b_{Ec}$ for even values of $J$, (10, 18, 26, 34, 42, 50, 58, \ldots)b_{Ec}$ for odd values of $J$. The peaks near zero are an artifact.

4.2. Molecular alignment observation with arbitrary orientations of pump and probe polarizations

In this section we consider molecular alignment with arbitrary mutual orientation of polarizations of the pump and probe pulses. The expectation value of the alignment for an arbitrary angle $\alpha$ is given by [34]

$$\langle \langle \cos^2 \theta \rangle \rangle (t) = \frac{1}{2} 3 \cos^2 (\alpha - 1) \langle \langle \cos^2 \theta \rangle \rangle (t) + \frac{1}{2} \sin^2 \alpha,$$  \hspace{1cm} (9)

where $\langle \langle \cos^2 \theta \rangle \rangle (t)$ is the thermal averaging of the degree of alignment (see Eq. (4)), $\theta'$ is the angle between molecular axis and polarization of the probe beam and $\alpha$ is the relative angle between the polarizations of pump and probe pulses.

For the parallel polarizations, $\alpha = 0$, we have $\langle \langle \cos^2 \theta' \rangle \rangle (t) = \langle \langle \cos^2 \theta \rangle \rangle (t)$ and for the perpendicular polarizations $\alpha = 90^\circ$, $\langle \langle \cos^2 \theta' \rangle \rangle (t) = \frac{1}{2} [1 - \langle \langle \cos^2 \theta \rangle \rangle (t)]$, which has obviously opposite phase as a function of $t$ for the full revival of $N_2$, as seen in Fig. 4. Indeed, the full revival signal shows a minimum around 8.2ps (anti-alignment) and a maximum around 8.35ps (maximal alignment) while at $\alpha = 90^\circ$ the full revival shows a maximum around 8.2ps (maximal alignment) and a minimum (anti-alignment) around 8.35ps. We can also see that the modulation depth for $\alpha = 90^\circ$ is smaller than the one for $\alpha = 0^\circ$. In addition, the measured molecular alignment degree of the revival with parallel polarizations was about twice the one with perpendicular polarizations, which is consistent with the fact that $\langle \langle \cos^2 \theta \rangle \rangle + 2 \langle \langle \cos^2 \theta' \rangle \rangle = 1$. 

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Fig. 4. Full revival of N\textsubscript{2} for parallel, $\alpha = 0^\circ$, and perpendicular, $\alpha = 90^\circ$ pump and probe polarizations. Red circles depict the measured probe beam power, and the black solid line shows the calculated nonlinear refractive index change. The data was normalized to the magnitude of the parallel polarization signal.

Fig. 5. Experimental (top) and theoretical (bottom) quantum carpets of a rotational full revival around 8.3ps.

In order to investigate how the structure of the rotational full revival changes with polarization angle \( \alpha \), we ran the experiment for a series of pump-probe delay scans with different pump pulse polarization angles with respect to the horizontally polarized probe pulse. The resulting structure of such a mapping of the rotational wave packet, the so-called “quantum carpet” [28]) is shown in Fig. 5. The theoretical results are calculated by using Eq. (9). As can be seen from the calculated quantum carpet in Fig. 5, there is an angle at which the expectation value of the alignment is the same for all delay times. This angle, as follows from Eq. (9), is given by $3 \cos^2 \alpha - 1 = 0$, i.e. $\alpha_c = 55^\circ$. We can see that this conclusion agrees well with our experiment data, given in Fig. 5. In Fig. 6, we plotted the modulation amplitudes $A_1 - A_0$, $A_2 - A_0$, and $A_1 - A_2$, where $A_1$, $A_0$, and $A_2$ are the probe beam powers measured at the alignment, at the random molecular orientations (no alignment), and at the anti-alignment, respectively, as shown in the inset of Fig. 6. The modulation $A_1 - A_2$ peaks at $\alpha = 0^\circ, 180^\circ$, and $360^\circ$ and reaches minima at $\alpha = 90^\circ$ and $270^\circ$, respectively. The $\alpha$-dependent modulation shows the power is enhanced at the alignment where molecules are...
parallel to the probe pulse field polarization and suppressed at the anti-alignment where molecules are perpendicular to the probe pulse field polarization. As follows from Fig. 5 and Fig. 6, the modulation phase is reversed at $\alpha = 55$. We note that the existence of angle $\alpha$, where the signal is independent of the time delay, is a specific signature for the $\sigma_g$ symmetry of the active molecular orbitals of nitrogen molecule [54].

![Graph showing experimental variations of $A_1 - A_0$ (blue square), $A_2 - A_0$ (black circle), and $A_1 - A_2$ (red triangle) as a function of the angle between the pump and probe field directions, $\alpha$, around full revival for N$_2$, where $A_1$, $A_0$, and $A_2$ are determined as shown in the inset, and the solid line stands for the variation of $A_1 - A_2$ which is calculated for the same conditions used in the experiment.]

A polar plot presented in Fig. 7 shows how the molecular alignment changes at the maximal alignment delay (8.35ps) and anti-alignment delay (8.15ps) as the angle of the polarization of the pump pulse was varied in experiment with respect to the polarization angle of the probe pulse that was fixed. The molecules are maximally anti-aligned along the polarization of the probe pulse at $\alpha = 90^\circ, 270^\circ$ simultaneously with the expected decrease of the refractive index around 8.15 ps, and they are maximally aligned along the polarization of the probe pulse at $\alpha = 0^\circ, 180^\circ$ where the refractive index increases around 8.35ps.

![Polar plots showing alignment signals at delay times within the full revival as functions of the relative angle between pump and probe polarizations. Molecules are maximally anti-aligned (blue, showing negative change of the signal) for 8.15 ps delay at $\alpha = 90^\circ, 270^\circ$ and aligned for 8.35 ps delay (red, showing positive change of the signal) at $\alpha = 0^\circ, 180^\circ$.]

The series of plots presented in Figs. 8 and 9 shows similar results of rotational half revival and first-quarter revival, respectively. For the half rotational revival, the molecules are aligned along the polarization of the probe pulse, where the refractive index increases at 4 ps, and they are aligned perpendicular to this direction with a decrease of the refractive index.
around 4.15 ps, as seen in Fig. 9. However, at the half revival the change of the alignment expectation comes with the opposite sign compared to the full revival.

Fig. 8. Experimental (top) and theoretical (bottom) quantum carpets of a rotational half revival around 4.1ps delay.

Fig. 9. The polar plots show alignment signals at delay times within the half revival as functions of the relative angle between pump and probe polarizations. Molecules are maximally aligned (red) at 4ps for $\alpha = 0, 180^\circ$ and anti-aligned (blue) at 4.15ps for $\alpha = 90^\circ, 270^\circ$.

At quarter revival the phase in the rotational wave packet depends on the parity of $J$-state. As was discussed earlier, the even and odd states have their phases shifted by $\pi$, and therefore they interfere destructively. Since the relative ratio of the statistical weights of even-$N_2$ versus odd-$N_2$ states is 2:1, their contributions do not cancel completely each other, but the signal has a reduced amplitude in comparison to the signal at the full and half revivals, as is observed in the experiment as in Fig. 10.
The series of polar plots presented in Fig. 11 shows how the molecular alignment changes with respect to the variable angle of the pump pulse around the first quarter revival time. Again due to the opposite contributions of the even and odd states they partially cancel each other, and therefore the molecular alignment signal is partially reduced compared to the full and half revivals. The molecules are maximally aligned along the polarization of the probe pulse with the simultaneous increase of the refractive index at $1.8\text{ps}$ and $2.2\text{ps}$ for $\alpha = 0^\circ, 180^\circ$, and maximally anti-aligned with a decrease of the refractive index at $2.2\text{ps}$ for $\alpha = 90^\circ, 270^\circ$.

5. Conclusions

In a simple set-up based on the interaction between a probe pulse and molecules pre-aligned by a pump pulse we implemented an experiment to study molecular alignment wakes of femtosecond laser pulses by modulation of the probe pulse. The variations of the transmitted probe pulse were explained by the induced intensity-dependent variations of the imaginary part of the refractive index. Theoretical calculations of nonadiabatic alignment by the pump pulse agreed well with experimentally measured signals. Both results have shown agreement in the periods, shape and magnitude of the revival signals at full, half and quarter revivals of nitrogen. The timing of revival events of the experimental and calculated values matched within the temporal error of the experimental conditions. In addition, we mapped ultrafast rotational wave packets as a function of the delay and polarization angle between the pump and probe pulses (i.e. experimentally obtained "quantum carpet") by using probe pulse power modulation to directly reconstruct the molecular alignment revivals in nitrogen. The experimental results of mapping rotational wave packets are also compared with quantum
mechanical calculations of the alignment parameter, and the results indicate that calculations describe all major experimentally observed features. Beyond understanding the dynamics of molecules interacting with ultrafast laser pulses, this information is applicable to any mechanism dependent on the molecular alignment. The results of the quantum carpet measurements illustrate that a room-temperature ensemble of molecule can be organized into an ordered state, which allows time- and energy-resolved measurements of the molecular rotational motion with spectroscopic accuracy. Besides, the proposed technique of probing molecular alignment can be easily implemented in a typical ultrafast laser facility and represents an important step to extend the experimental interest to other gases and also more complex systems. In addition, we have shown the variations of the femtosecond pulse duration that interacted with the aligned nitrogen molecules, and this effect is of interest for tailoring laser pulses.

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