Optics of a Gas of Coherently Spinning Molecules

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We consider optical properties of a gas of molecules that are brought to fast unidirectional spinning by a pulsed laser field. It is shown that a circularly polarized probe light passing through the medium inverts its polarization handedness and experiences a frequency shift controllable by the sense and the rate of molecular rotation. Our analysis is supported by two recent experiments on the laser-induced rotational Doppler effect in molecular gases, and provides a good qualitative and quantitative description of the experimental observations.

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When a circularly polarized photon is scattered forward from an anisotropic body, its polarization handedness may be inverted, and the scattering is accompanied by an exchange of angular momentum \( \Delta L = 2\hbar \) between the photon and the body. For a body rotating at a frequency \( \Omega \) much smaller than the light frequency, the kinetic energy of rotation is modified by \( \Omega \Delta L = 2\hbar \Omega \). This should be compensated by the photon energy change, therefore the frequency of the scattered photon becomes shifted by \( 2\hbar \Omega \). This phenomenon, called the rotational Doppler shift \([1, 6]\) is a macroscopic classical analog of the rotational Raman effect \([6]\). It has been observed in the past by using mechanical rotation of optical elements \([7–10]\) and electro-optic effects in a nonlinear crystal subject to a rotating microwave electric field \([11]\).

In recent years there has been an ever-growing interest in aligning gas molecules by ultra-short laser pulses (for recent reviews see \([12, 13]\), earlier developments are described in \([14]\)). The research resulted in numerous achievements ranging from differentiation of molecular species through enhancement of filamentation effects to high harmonic generation control and attosecond pulse generation. Several methods have been suggested and demonstrated for converting the transient molecular alignment into a concerted unidirectional molecular rotation, including the techniques of ‘optical centrifuge’ \([15–17]\), ‘molecular propeller’ \([18–20]\), and ‘chiral train’ of laser pulses \([21, 23]\).

In this theoretical paper we investigate the propagation of light through a gas of unidirectionally rotating molecules, analyze polarization and spectral changes due to the energy and angular momentum exchange with the gas, and demonstrate that the light may experience a THz-range rotational Doppler frequency shift under experimentally feasible conditions. Our analysis considers in a unified way two recent experiments on the optics of gases of coherently spinning molecules \([24, 25]\) whose results are in accord with our theory.

Consider an ensemble of unidirectionally rotating linear molecules prepared by one of the above techniques \([15, 23]\). The simplest of them (‘molecular propeller’ \([18–20]\)) uses a sequential excitation by two delayed pump pulses with different linear polarizations. The first pulse aligns the molecules and the second one applies a biased torque to them thus causing the unidirectional rotation. We denote the molecular polarizability anisotropy by \( \Delta \alpha = \alpha_\parallel - \alpha_\perp \) (\( \alpha_\parallel, \alpha_\perp \) are the polarizability values along and perpendicular to the molecular axis, respectively). The pump pulses are assumed to be collinear and to propagate at the same speed, \( c/n \), as in the undisturbed and unaligned medium. Here \( c \) is the speed of light, \( n = \sqrt{1 + N\alpha \epsilon_0^{-1}} \) is the refractive index, \( \bar{\alpha} = (\alpha_\parallel + 2\alpha_\perp)/3 \) is the orientation-averaged molecular polarizability, \( N \) the concentration of the molecules, and \( \epsilon_0 \) is the vacuum permittivity. For undepleted pump pulses (as is the case for nonresonant excitation in transparent gases), the rotational dynamics of molecules at any given distance down the propagation line depends only on the time elapsed since the pulsed pump acted at that same location. Following the excitation, the molecules continue their field-free rotation, each at a constant angular velocity.

The electric field \( \mathbf{E}_i \) of an incident probe pulse follows Maxwell’s equations

\[
\frac{\partial}{\partial z} \mathbf{E}_i - \frac{1}{c^2} \frac{\partial}{\partial t} \mathbf{E}_i = \frac{1}{c^2} \frac{\partial}{\partial t} (\nabla \mathbf{E}_i),
\]

where \( \nabla \) is the electric susceptibility tensor of the medium. In the paraxial approximation the only significant field components are those perpendicular to the propagation axis \( z \). We express the susceptibility in the basis of circular polarization (CP) states,

\[
\chi(z, t) = N \left( \bar{\alpha} - \frac{\Delta \alpha}{2} \left( \cos^2 \theta_0 - \frac{1}{3} \right) \right) I + \frac{N \Delta \alpha}{2} \left( \frac{\rho^*}{\rho} G \right) ;
\]

\[
\rho = \langle \sin^2 \theta \cos 2\varphi \rangle ;
\]

\[
G = \langle \cos^2 \theta_0 - \cos^2 \theta \rangle .
\]

Here \( I \) is the unity matrix, and the averaging is made over all the molecules in a unit volume. We use the standard spherical angles \( \theta \) and \( \varphi \) to denote the instantaneous orientation of the molecules (the polar angle \( \theta \) is measured...
from the propagation direction $z$). The angle $\theta_0$ denotes the angle at the moment of the pulse arrival to the molecule’s location. The molecular rotation frequency is assumed to be small compared with the optical carrier frequency $\omega$, thus allowing the calculation of the susceptibility by the coordinate transformation to the molecules’ rotating frame.

In what follows, we consider a delayed probe pulse, $\mathbf{E}_i = \mathcal{E}_i (z,t) \exp i \omega_0 (t - z/\nu)$, with a slowly varying envelope $\mathcal{E}_i (z,t)$ of two CP components propagating collinearly with the pumps. We use the first, time-independent, term of the polarizability in Eq. (2), to define the velocity value $V_i = c \left( 1 + \epsilon_0^{-1} N \left( \pi - \Delta \alpha/2 (\cos^2 \theta_0 - 1/4) \right) \right)^{-1/2}$ that is the common term for both CP components. We rearrange Eq. (1) by neglecting the second order derivatives, and transforming to the probe’s time frame $(z', \tau) \equiv (z, t - z/\nu)$:

$$
\partial_t \mathcal{E}_i = -i \beta_i \left( \frac{G \rho^*}{G} \right) \mathcal{E}_i + 2 \frac{\beta_i}{\omega_i} \partial_\tau \left[ \left( \frac{G \rho^*}{G} \right) \mathcal{E}_i \right] \quad (3)
$$

$$
\beta_i = \frac{\mu_0 N \Delta \alpha \omega_i V_i}{4},
$$

where $\mu_0$ is the vacuum permeability. Here, $\rho$ and $G$ (and all other time-varying quantities) depend only on time $\tau$, elapsed since the pumps arrived at each location. This is justified as long as the pump-probe speed difference is small enough so that the probe ‘surfs’ on the seemingly unchanging wake of the pump throughout the interaction length, $l$ (i.e., when $l \ll \Delta t_{ai} c / (N |\Delta \alpha| \epsilon_0^{-1})$, where $\Delta t_{ai}$ is the typical time scale of the molecular alignment dynamics).

We use a basis transformation $\mathcal{R}$ to diagonalize the matrix that appears in Eq. (3):

$$
\left( \begin{array}{cc} G \rho^* \\ G \\ \rho \\ G \end{array} \right) = \left( \begin{array}{cccc} -\frac{\rho^*}{|\rho|} & \frac{\rho}{|\rho|} & 0 & 0 \\ 0 & 0 & G + |\rho| & 0 \\ 0 & 0 & G - |\rho| & \frac{\rho}{|\rho|} \\ 0 & 0 & -\frac{\rho^*}{|\rho|} & \frac{\rho}{|\rho|} \end{array} \right) \equiv \mathcal{R} (\tau) \cdot \mathcal{K} (\tau) \cdot \mathcal{R}^{-1} (\tau).
$$

Here, again, $\mathcal{R}$ and $\mathcal{K}$ are functions of $\tau$ only. Physically, the transformation $\mathcal{R}$ defines the instantaneous birefringence axes of the medium. We present the two components of the pulse in the $\mathcal{K}$ eigenvectors basis as $(\mathcal{E}_+ \mathcal{E}_-)^T = \mathcal{R}^{-1} \mathcal{E}_i$. Eq. (3) may be replaced by two scalar equations:

$$
\left[ \partial_\tau - 2 \frac{\beta_i}{\omega_i} (G \mp |\rho|) \partial_\tau \right] \mathcal{E}_\pm = -i \beta_i (G \mp |\rho|) \mathcal{E}_\pm + \quad (4)
$$

$$
+ 2 \frac{\beta_i}{\omega_i} [\partial_\tau (G \mp |\rho|)] \mathcal{E}_\pm + \quad (4)
$$

$$
+ i \beta_i \frac{\Phi}{\omega_i} (G \pm |\rho|) \mathcal{E}_\pm ,
$$

where $\Phi$ is the argument of $\rho \equiv |\rho| \exp i \Phi$. Equations (4) (or Eqs. (3)) describe a rich variety of phenomena in a time-dependent birefringent medium. In particular, the second term on the rhs of Eq. (4), is responsible for amplification/attenuation of the field amplitudes $\mathcal{E}_\pm$ in a non-stationary anisotropic medium with ‘non-rotating’ birefringence axes. The third term on the rhs of Eq. (4) describes a non-adiabatic coupling between the $\mathcal{E}_\pm$ amplitudes in a medium with rotating birefringence, which also results in a change of the CP amplitudes (see, e.g. [23]). However, the cumulative amplitudes’ change due to these terms is small as long as the difference in propagation time of the two field components through the medium is smaller than the molecular alignment time scale ($t \ll \Delta t_{ai} c / (N |\Delta \alpha| \epsilon_0^{-1})$), and as long as the frequency of the birefringence axis rotation is slower than the optical frequency, $|\Phi| \ll \omega$. Under these conditions, which prevail in recent experiments [24,25], we may neglect these terms.

The remaining uncoupled equations have a simple solution, which we combine and obtain the total CP field at location $z$ as a function of the incoming field envelope $\mathcal{E}_i (z = 0)$:

$$
\mathcal{E}_i (z) \approx e^{i \omega_0 \tau} \exp (i \beta_i G z) \times
$$

$$
\left[ \cos (\beta_i |\rho| z) I + i \sin (\beta_i |\rho| z) \left( \begin{array}{cc} 0 & e^{-i \Phi} \\ e^{i \Phi} & 0 \end{array} \right) \right] \mathcal{E}_i (0).
$$

This expression describes a Rabi-like oscillation between the two CP components. We identify the $z$-dependent phase modulation terms, especially the exponent containing $G$. The rotational Doppler shift effect is described by the exponents of $\Phi$ in the off-diagonal elements of the matrix in the right hand side of Eq. (5). To validate our solution, we have analyzed polarization and spectral transformations of a probe pulse for various medium-preparation scenarios (see below) and found a good agreement between the results based on the analytical Eq. (5) and those obtained by solving Eq. (4) numerically (finite difference time domain calculations).

Next we discuss the effect of specific molecular excitation scenarios on the probe pulse. We first examine the simplest model case in which the molecular orientation is restricted to be perpendicular to the laser propagation direction ($z$ axis). We assume that when the maximum of the probe pulse arrives, the molecules are perfectly aligned and have a normal distribution of angular velocity $\dot{\varphi}$ with a non-zero average $\Omega$ and a standard deviation $\sigma$. It can be shown that in this case $|\rho| = \exp (-2 r^2 \sigma^2)$, $\Phi = 2 \Omega t$ and $G = 0$. For a left-CP input field $\mathcal{E}_L (z = 0)$, Eq. (5) provides the following expression for the generated right-CP field at the exit of the medium:

$$
E_R (z) \approx i \sin \left( \frac{\beta_i e^{-2 r^2 \sigma^2}}{2} \right) e^{i (\omega + 2 \Omega) t} \mathcal{E}_L (0).
$$

The apparent $+2\Omega$ frequency shift in the generated field
is inverted when the input field has a right-CP handedness. Moreover, when the angular velocity deviation $\sigma$ is zero (all the molecules rotate in unison, and with the same speed), Eq. (6) shows a simple Rabi-type oscillation and frequency shift that is consistent with that of light propagating through a rotating waveplate [8, 27]. Our simplified classical model of a "molecular waveplate" corresponds to experiment [28], in which highly efficient single-sideband frequency conversion was indeed observed via coherent driving of a single rovibrational Raman transition in molecular deuterium.

We proceed now to a more sophisticated 3D model of molecules brought into fast unidirectional rotation by a pair of delayed pump pulses according to the ‘molecular propeller’ scheme [18, 20]. To calculate the $\rho$ and $G$ time-dependent values, we used both classical Monte Carlo simulation [20] (for short pump-probe delays) and full quantum mechanical calculation (when the delay becomes comparable to the molecular rotational revival time). In the latter case, we analyzed the rotational dynamics of quantum wave packets and averaged over the thermal distribution of the initial rotational states (similarly to [18]).

Figure 1 depicts the calculated frequency content of the output pulse of inverted circular polarization for different time delays between the CP probe and the last pump pulse (left panels), as compared to the recent experiment [24] (right hand side). This example corresponds to nitrogen molecules of air at ambient conditions, and the delays are chosen around the half-revival time of the nitrogen, $T_\text{rev} = 8.3 \text{ ps}$ [14]. The kick strength [29] of each of the pump pulses is $P = 5$, close to the estimated experimental value. Figure 1a shows a spectrogram for a control case in which only a single pump pulse is employed. The vertical line marks the central wavelength of the incident pulse. A considerable spectral broadening is observed in the half-revival region (both in simulations and in the experiment) because of the phase modulation effect, but no visible spectral shift is present. However, if unidirectional rotation is present (see the middle and the lower panels of Fig. 1), the spectrograms are shifted to the red or to the blue, depending on the relative handedness of the probe field polarization and induced molecular rotation.

In our simulation, the rotational Doppler shift reaches the level of about 5 THz. For a 800 nm probe pulse this translates to the wavelength deviation of about $\sim 10$ nm, close to the spectral width of pulses used in experiments [24]. The predicted value of the shift and its direction are in a good agreement with the reported experimental observations (see Figs. 1a, c).

As an additional and independent test of our theory, we consider another recent experiment [25], in which unidirectionally rotating $O_2$ molecules were produced using the ‘optical centrifuge’ scheme. In that experiment, molecules were optically spun at a continuously increasing rotational frequency, up to $J \sim 69h$ after which the centrifuge was abruptly switched off (only odd values of $J$ are allowed for $^{16}O_2$ molecule because of its nuclear spin statistics). The optical properties of the molecular medium were probed by a delayed CP probe pulse during the centrifuge operation, and after its termination.

To model this situation, we analyzed the time dependence of the functions $G$ and $\rho$ during the acceleration period (when the molecules are trapped by the centrifuge field) both classically and quantum mechanically, with a good agreement between the two approaches. The long-time evolution of these functions after the driving field was cut off and acceleration had stopped was treated quantum mechanically, in order to account for quantum revivals of the released rotational wave packets. Figure 2a shows our results for the spectrum of the oppositely circularly polarized signal at the output of the medium as a function of the probe delay with respect to the start of the centrifuge. The calculated signal shows good qualitative and quantitative agreement with the results of the reported experimental observations [25] (see Fig. 2b). At the acceleration stage, it exhibits linearly growing frequency shift corresponding to twice the instantaneous rotation frequency of the centrifuge. In the field-free regime (after the end of the centrifuge at $\sim 60$ ps), the excited rotational wavepacket produces a revival oscillatory pattern of the signal strength, as shown in the insets of Fig. 2. The revival period changes with time because of the centrifugal distortion effect in the molecular rota-

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**Figure 1.** (Color online) Spectrum of the output field of inverted circular polarization vs. pump-probe delay for $^{14}N_2$ molecules brought to unidirectional rotation by the two-pulse “molecular propeller” scheme. Color depicts the magnitude of the signal (arbitrary scaling). Left column shows calculated spectrum, the right one presents experimental data from [24] (with permission). Panel (a) displays results for a control single-pulse excitation for which no chiral effect exists. Panel (b) corresponds to molecules having the same sense of rotation as the electric vector of the input CP pulse, panel (c) presents results for the opposite sense of molecular rotation.
Figure 2. (Color online) (a) Calculated spectrum of the output field of inverted circular polarization vs. probe delay for $^{16}$O$_2$ molecules spun by the ‘optical centrifuge’ to $J \sim 69 \hbar$. (b) The corresponding experimental results (from [25], with permission). The insets show the signal intensity (a.u.) after the end of centrifugation.

The exact position of the revival peaks depends on the relative phases accumulated by different rotational states during the centrifugation and in the process of the release from the centrifuge [25]. We matched our results to the experiment by tuning the phases of different states of the final rotational wavepacket to fit the position of a single, arbitrarily chosen peak of the signal experimentally recorded near $\sim 300$ ps delay. As a result, a very good agreement between the calculated and measured revival signals has been achieved in the whole post-centrifugation region (compare the insets of Figs. 2a and 2b).

Finally, we discuss an additional manifestation of the chirality transfer from the molecular medium to a probe light, when the input probe is linearly polarized. The latter may be regarded as a pair of circularly polarized pulses of opposite handedness. When the probe encounters a gas of unidirectionally rotating molecules, each of these CP components partially transforms into a ‘daughter’ CP pulse of opposite chirality. The two mirror CP daughter pulses appear in phase, they have opposite rotational Doppler frequency shifts but equal amplitudes, thus they effectively combine into a linearly polarized field. However, the polarization direction, determined by the relative phase between the two pulses, rotates with time at twice the mean frequency of the molecular spinning, resulting in a wave of autonomously rotating linear polarization (WARP) featured in Fig. 3. This kind of polychromatic light has been created in the past [30] using a mechanically rotating waveplate. The mechanisms considered in our paper allow for generating the WARPs with the polarization rotation frequency which is many orders of magnitude higher.

In conclusion, we presented a theoretical analysis of the optical properties of a gas of unidirectionally rotating molecules, and showed that such a coherent collective spinning substantially shifts the spectrum of a CP light pulse passing through the medium. The direction of the shift is determined by the relative handedness of the molecular rotation and the CP pulse, and the shift value is controlled by the rate of molecular rotation. Our treatment considers in a unified way two recent experiments on the optics of gases with unidirectionally spinning molecules [24, 25], and provides a good qualitative and quantitative description of the measurement results. We also discussed using the molecular-induced frequency shift to prepare a pulse whose linear polarization continuously rotates at a THz-range speed. This ‘twisted polarization’ mode may become an interesting and useful addition to the gallery of femtosecond shaped pulses, especially in view of high and tunable rotation frequency, and relatively simple preparation method.

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