Magneto-optical properties of paramagnetic superrotors

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We study the dynamics of paramagnetic molecular superrotors in an external magnetic field. Optical centrifuge is used to create dense ensembles of oxygen molecules in ultra-high rotational states. It is shown for the first time, that the gas of rotating molecules becomes optically birefringent in the presence of magnetic field. The discovered effect of “magneto-rotational” birefringence indicates preferential alignment of molecular axes along the field direction. Our experimental observations are supported by numerical calculations and explained by means of an intuitive qualitative model, in which the influence of the applied magnetic field on the distribution of molecular axes is mediated by the spin-rotation coupling. We show the magnetic reversal of the rotational Raman signal, as well as investigate the robustness of the induced magneto-rotational birefringence with respect to collisions.

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Control of molecular rotation with electromagnetic fields of various types and geometries has become a powerful tool in a number of rapidly growing fields of molecular science (for a recent review, see Ref.1). From attosecond high-harmonic spectroscopy[2, 3] and photoelectron spectroscopy[4] to controlling molecular interactions with atoms[5], molecules[6] and surfaces[7, 8], to altering molecular trajectories[9, 10], the ability to align either the frames of rotating molecules or their angular momenta is one of the key requirements.

Sequences of linearly polarized ultrashort laser pulses have been successfully used for controlling molecular rotation[11–14]. This excitation scheme, however, is limited to low rotational levels because of the detrimental effects of multi-photon ionization at high laser intensities. The rotation of polar or paramagnetic molecules can be harnessed by static electric or magnetic field, respectively [15, 16]. In both cases, an applied external field interacts with the permanent dipole moment of a molecule, hybridizing its rotational levels and creating pendular states in which the molecular axis is librating around the field direction[17]. The combination of static and optical fields has been suggested[18] and demonstrated[19, 20] as a means of enhancing molecular alignment beyond that achievable with a static field alone. All mentioned techniques rely on Stark or Zeeman shifts to exceed the energy separation of the rotational levels. As the latter grows rapidly with the rotational quantum number, these control schemes are also limited to rotationally cold ensembles.

In this work, we extend the reach of rotational control by static external fields to ultra-high rotational states. We use the method of molecular spinning in an optical centrifuge[21, 22] and exploit its capability to generate and control narrow rotational wave packets in extremely broad range of angular momenta[23]. We show for the first time that an external magnetic field, applied at 90 degrees to the axis of molecular rotation, results in a significant re-orientation of molecular axes.

A transparent physical mechanism of the observed phenomenon is proposed and confirmed by numerical calculations. Set to ultrafast uni-directional rotation, centrifuged diatomic molecules (known as molecular superrotors) exhibit high degree of planar confinement as their atomic nuclei are strongly localized in the plane perpendicular to the axis of the centrifuge. For a superrotor with a nonzero magnetic moment coupled to its internuclear axis, such planar distribution is converted to the molecular alignment along the direction of the applied field. We experimentally demonstrate this effect, hereafter referred to as “magneto-rotational”, by showing that a gas of oxygen superrotor in an external magnetic field of moderate strength (≈ 1 Tesla) exhibits strong linear birefringence. We study the decay of the observed magneto-rotational birefringence, as well as its dependence on the molecular angular momentum and the strength of the applied magnetic field.

The importance of accessing superrotor states for this study is twofold. First, the lifetime of the centrifuge-induced molecular rotation in dense media increases with the nuclear rotational quantum number \(N[24]\). Since high density is key for observing optical birefringence in gas samples, we benefit from the robustness of superrotors with respect to collisions. Second, the degree of molecular localization in the plane of rotation, generated by the centrifuge, also grows with increasing \(N\), making the magneto-rotational effects more pronounced.

The experimental setup is shown in Fig.1(a). A beam of femtosecond pulses from an ultrafast laser source (spectral full width at half maximum (FWHM) of 30 nm) is split in two parts. One part is sent to the “centrifuge shaper” which converts the input laser field into the field of an optical centrifuge (illustrated in the inset) according to the original recipe of Karczmarek et al. [25]. The centrifuge shaper is followed by a home built Ti:Sapphire multi-pass amplifier boosting the pulse energy to 50 mJ. The second (probe) beam is frequency shifted to 400 nm, spectrally narrowed to about 4 cm\(^{-1}\) (FWHM) with a
Oxygen molecules rotating with this frequency occupy rotational quantum states with $N = 71$. The absence of the opposite anti-Stokes Raman line indicates uni-directional molecular rotation[23].

When the magnetic field is turned on, the amplitude of the Rayleigh peak becomes much higher, corresponding to strong incoherent (hence, frequency-unsigned) magneto-rotational birefringence.Unlike the weak initial depolarization which has no preferential axis at zero field, the magnetically induced birefringence exhibits a well defined optical axis. The applied magnetic field also affects the coherent Raman sidebands. While the initial Raman peak falls off with increasing $B$-field, a weak anti-Stokes Raman line grows on the other side of the spectrum, reflecting molecular rotation in the opposite, with respect to the centrifuge, direction.

To understand the nature of the observed magneto-rotational effects in the gas of paramagnetic superrotors, we calculate the angular distribution of $O_2$ molecules subject to constant magnetic field. The interaction between the spins of the two unpaired electrons and the nuclear rotation results in the spin-rotation coupling, which splits each rotational level in three components characterized (Stokes) Raman peak. The former is a result of the depolarization of probe light due to the non-uniform (and randomly changing from pulse to pulse) distribution of molecular axes in the plane of rotation. The second component reflects coherent molecular rotation with an angular frequency of about 6 THz (half the Raman shift).

The main result of this work is shown in Fig.2, where the observed power spectrum of probe pulses, passed through the ensemble of centrifuged oxygen, is plotted as a function of the magnetic field strength. At zero field, the probe spectrum consists of two components: the frequency-unsigned Rayleigh line and the down-shifted (Stokes) Raman peak. The former is a result of the depolarization of probe light due to the non-uniform (and randomly changing from pulse to pulse) distribution of molecular axes in the plane of rotation. The second component reflects coherent molecular rotation with an angular frequency of about 6 THz (half the Raman shift).
by the total angular momentum \( J = N, N \pm 1 \). An applied \( B \)-field lifts the degeneracy of each level with respect to the projection \( M_J \) of \( J \) on the field axis. We calculate the energies \( E_{N,J,M_J}(B) \) of the magnetic sub-levels by numerically diagonalizing the electron-spin Zeeman Hamiltonian, starting from its matrix elements in Hund’s case (b) basis set \([N, S, J, M_J]\), with \( S = 1 \) being the total electronic spin.

Given the initial thermal ensemble, the centrifuge creates an incoherent mixture of three states \([N, S, J, M_J]\) with maximum projections \( M_J \) on the centrifuge direction. Using \( J \gg S \), we approximate the angular distribution of the state \([N, S, J, M_J]\) by the spherical harmonics \( Y_{J,M_J}(\theta, \phi) \). We verified this approximation by a more elaborate calculation of the exact angular distributions which will be described in a future publication. Using this approximation, the final angular distribution at time \( t \) is given as:

\[
\rho_N(\theta, \phi) \approx \sum_{J=N,N+1} \sum_{M_J} |c_{J,M_J}|^2 e^{iE_{N,J,M_J}(B)t/h} Y_{J,M_J}(\theta, \phi),
\]

where \( c_{J,M_J} \) are the wave function amplitudes in the coordinate frame with the quantization axis along the applied magnetic field. The results of our calculations for \( N = 59 \) are shown in Fig.3. A disk-like distribution at \( B = 0 \) (panel (a)) corresponds to the molecular rotation around the centrifuge propagation direction \( \hat{k} \), with the molecular axes isotropically distributed in the perpendicular \( yz \) plane. As seen in panel (b) of Fig.3, an applied magnetic field splits the disk into three components. In the majority of cases considered here, the coupling between the electronic spin and an ultrafast rotation of superrorors is stronger than its interaction with the external \( B \)-field. The perturbative effect of the latter on the precession of the spin around \( \hat{N} \) results in a clockwise (counter-clockwise) rotation of \( \hat{N} \) around \( \hat{B} \) for \( J = N-1 \) \((J = N+1)\) states and no rotation for \( J = N \) states. This leads to the anisotropic distribution stretched along \( \hat{z} \). In agreement with this model, a \( \cos^2(\theta_p) \) dependence shown in Fig.3(c) indicates the appearance of a well-defined anisotropy axis along the direction of the field, as expected from the geometry of the calculated distribution. We note that for stronger magnetic fields, the three spin states decouple from the molecular angular momentum and the physical picture changes; this scenario will be considered in a future publication.

We now proceed with the analysis of the temporal evolution of the birefringence signal, which we define as the difference between the amplitude of the Rayleigh peak with and without the applied magnetic field. Figure 3(a) shows this signal, measured at a fixed magnetic field of 2 Tesla, as a function of the probe time delay with respect to the angular distribution of the molecular axes for the rotational state with \( N = 59 \) at time \( t = 1 \) ns in an external magnetic field of 0 and 2 Tesla, respectively. (c) Birefringence signal (scaled to peak at 1) as a function of time.

\[ \text{FIG. 3: (a,b) Calculated angular distribution of the molecular axes for the rotational state with } N = 59 \text{ at time } t = 1 \text{ ns in an external magnetic field of 0 and 2 Tesla, respectively. (c) Birefringence signal (scaled to peak at 1) as a function of angle } \theta_p \text{ between the polarization of probe pulses and the magnetic field direction. Black circles: data taken at 2 T, } t = 1.5 \text{ ns, and } N = 95. \text{ Red curve is a fit to } \cos^2(\theta_p). \]
to the beginning of the centrifuge pulse. After a rapid initial growth, the magneto-rotational birefringence decays exponentially due to de-orienting collisions.

Truncating the centrifuge pulse in the centrifuge shaper so as to stop the accelerated rotation at different angular frequencies allows us to create rotational wave packets centered at different values of $N$ and study the dependence of the magnetic effect on the frequency of molecular rotation. The results are plotted in Fig.4(a) and indicate the decreasing decay rate of the magnetically induced birefringence with increasing $N$. One can also see that the birefringence signals reach their maximum values at different delay times: the higher the angular momentum, the slower the magnetic response.

To infer the mechanism of the observed decay, we compare it to the rate of rotational energy transfer due to collisions, analyzed in our recent study of oxygen superrotors[26]. For each value of $N$, the rate of the $N$-changing collisions is indicated by a dashed line originating from the peak of the corresponding curve. The similarity of the two time scales points at the inelastic collisions as the main cause for the decay of the magneto-rotational birefringence. For all $N$’s except $N = 13$, the birefringence signals decrease slower than the rotational population of the corresponding state. This fact suggests that the centrifuge-induced directionality of molecular rotation is the reason behind the slow decay of the observed magnetic birefringence. This is consistent with the recently found propensity of molecules to keep the orientation of their angular momentum in the course of inelastic collisions (“gyroscopic effect”), as reflected in the relaxation dynamics of the laser induced molecular alignment signals[27, 28].

At low rotational frequencies ($N = 13$), the gyroscopic effect is weaker and the directionality of rotation becomes as susceptible to collisions as the rotational energy itself (blue curves in Fig.4(a)). The other end of the scale ($N \approx 100$) corresponds to the limit of adiabatic collisions, where the rate of rotational decoherence approaches its asymptotic value and no longer depends on the rotational quantum number. Found in Ref. 26 and attributed to spin-flipping collisions, i.e. collisions which lead to transitions between the $J = N, N \pm 1$ states within a single $N$ manifold, this decoherence rate is indicated by the black dashed line in the upper right corner of Fig.4(a).

The dependence of the magneto-rotational birefringence on the strength of the applied magnetic field is shown in Fig.4(b). After the initial growth with increasing $B$, the signal saturates. For different rotational frequencies, the saturation occurs at different field amplitudes. Slower superrotors do not only require shorter time to respond to the external magnetic field, but also need weaker fields to reach the plateau. Our numerical estimates of the birefringence signal, based on the calculated angular distributions of molecular axes (see Fig.3), successfully reproduce our experimental findings, showing qualitatively similar behavior.

Angular distributions are also instructive in the interpretation of the magnetic reversal of the coherent Raman scattering. The latter effect is clearly seen in Fig.2 as the appearance of a weak Raman line with a frequency shift corresponding to the molecular rotation in the direction opposite to the initial, centrifuge-induced rotation. Indeed, the precession of the two parts of the angular distribution around the applied magnetic field, as described earlier in the text, results in a small negative component in the projection of the molecular angular momentum on the centrifuge axis. The above mentioned effects of magnetic saturation and magnetic reversal will be further analyzed in the future publication.

To summarize, we showed that strong planar confinement ($\langle \cos \theta^2_{\parallel, z} \rangle = 0.5$) of paramagnetic molecular superrotors can be converted into an anisotropic angular distribution ($\langle \cos \theta^2_{\parallel} \rangle < 0.5, \langle \cos \theta^2_{\perp} \rangle = 0.5$) by means of external magnetic field. Here, $\theta_\alpha$ is the angle between the molecular axis and unit vector $\hat{\alpha}$, and $\langle \cdot \rangle$ represents ensemble averaging. Our experimental and theoretical analysis confirms the mediating role of an electronic spin in the demonstrated new scheme of rotation control. The effect can be used for fast switching of optical birefringence in gases, as well as for studying aligned molecules in ultra-high rotational states. Magneto-rotational birefringence, investigated in this work, also offers a way of exploring the effect of collisions on the directionality of molecular rotation in dense media.

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