Coherent spin–rotational dynamics of oxygen superrotors

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Abstract
We use state- and time-resolved coherent Raman spectroscopy to study the rotational dynamics of oxygen molecules in ultra-high rotational states. While it is possible to reach rotational quantum numbers up to $N \approx 50$ by increasing the gas temperature to 1500 K, low population levels and gas densities result in correspondingly weak optical response. By spinning $O_2$ molecules with an optical centrifuge, we efficiently excite extreme rotational states with $N \leq 109$ in high-density room temperature ensembles. Fast molecular rotation results in the enhanced robustness of the created rotational wave packets against collisions, enabling us to observe the effects of weak spin–rotation coupling in the coherent rotational dynamics of oxygen. The decay rate of spin–rotational coherence due to collisions is measured as a function of the molecular angular momentum and its dependence on the collisional adiabaticity parameter is discussed. We find that at high values of $N$, the rotational decoherence of oxygen is much faster than that of the previously studied non-magnetic nitrogen molecules, pointing at the effects of spin relaxation in paramagnetic gases.

Keywords: molecular superrotors, spin–rotation coupling, optical centrifuge, quantum decoherence, rotational spectroscopy

Rotational spectroscopy of molecular oxygen, one of the most abundant molecules in the Earth’s atmosphere, is key to many studies in physics and chemistry, from atmospheric science and astronomy [1] to thermochemistry and combustion research [2–5]. Among simple diatomic...
molecules, O$_2$ stands out because of its non-zero electron spin (S = 1) in the ground electronic state, X$^3\Sigma^\text{−}$. The interaction between the spins of the two unpaired electrons and the magnetic field of the rotating nuclei results in the spin–rotation (SR) coupling on the order of a few wave numbers, which grows with increasing nuclear rotation quantum number $N$ [6]. This coupling of the electron magnetism with molecular rotation, readily controllable with laser light, offers new opportunities for controlling molecular dynamics in external magnetic fields [7].

SR coupling splits each rotational level in three (figure 1(a)), with the total angular momentum $J = N + 1, N, N − 1$, respectively. Three strongest Raman transitions (out of the total six allowed by the selection rules) corresponding to the $S(N')$ branch are shown and labeled according to the participating $J$-states. Figure 1(b) shows the dependence of the three Raman frequencies ($\Omega_k$ for $S_k$ line) on the rotational quantum number.

![Figure 1](image.png)

In this work we employ the technique of an optical centrifuge [20, 21] to excite oxygen molecules to ultra-high angular momentum states, reaching rotational quantum numbers as high

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Similarly to our previous studies of nitrogen superrotors [17], we observe that the lifetime of rotational coherence in oxygen becomes substantially longer at high $N'$s, making the detection of spin–rotational oscillations possible even at the pressure of 1 atm. By lowering the pressure, we observe SR dynamics in the broad range of angular momentum, $3 \leq N \leq 109$. We measure the decay rate of the SR oscillations due to $O_2$–$O_2$ collisions and analyze its dependence on $N$ using the adiabaticity correction factor from the energy corrected sudden (ECS) model of rotational energy transfer. In contrast to other experimental methods, our ability to vary the speed of molecular rotation without changing the temperature of the gas allows us to reach the adiabatic limit of rotational relaxation, when the period of molecular rotation becomes shorter than the collision time [17].

The experimental setup is similar to that used in our original demonstration of molecular superrotors [16]. As shown in figure 2(a), a beam of femtosecond pulses from a regenerative chirped pulse amplifier (spectral full width at half maximum (FWHM) of 30 nm, chirped pulse length 140 ps, FWHM) 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. Shown in figure 2(b), the centrifuge shaper is implemented according to the original recipe of Karczmarek et al [22]. It consists of a grating-lens pair which disperses the spectral components of the pulse in space. A pick-off mirror, placed in the Fourier plane of the lens, splits the beam in two parts which are sent to two ‘chirp boxes’, CB1 and CB2. CB1 preserves the frequency chirp of the input pulse, whereas CB2 changes it to the chirp of an opposite sign and same magnitude. The centrifuge shaper is followed by a home built Ti:Sapphire multi-pass amplifier boosting the energy of each chirped pulse up to 30 mJ. The two amplified pulses are then circularly polarized in an opposite direction with respect to one another and spatially re-combined into a single beam.
Optical interference of the two oppositely chirped and circularly polarized components produces the field of an optical centrifuge, schematically illustrated in the inset to figure 2(a). Centrifuge pulses are about 100 ps long, and their linear polarization undergoes an accelerated rotation, reaching the angular frequency of 10 THz by the end of the pulse. The second (probe) beam passes through the standard 4f Fourier pulse shaper employed for narrowing the spectral width of probe pulses down to 3.75 cm\(^{-1}\) (FWHM). The central wavelength of probe pulses is shifted to 398 nm by means of the frequency doubling in a nonlinear BaB\(_2\)O\(_4\) crystal.

As demonstrated in our previous work [16], the centrifuge-induced coherence between the states \(|J, m = J\rangle\) and \(|J + 2, m = J + 2\rangle\) (where \(m\) is the projection of \(\vec{J}\) on the propagation direction of the centrifuge field) results in the Raman frequency shift of the probe field (which can also be viewed as the rotational Doppler effect [23]). From the selection rule \(\Delta m = 2\) and the conservation of angular momentum, it follows that the Raman sideband of a circularly polarized probe is also circularly polarized, but with an opposite handedness. Due to this change of polarization, the strong background of the input probe light can be efficiently suppressed by means of a circular analyzer, orthogonal to the input circular polarizer (CA and CP, respectively, in figure 2(a)).

The Raman spectrum of the probe pulses scattered off the centrifuged molecules is measured with an f/4.8 spectrometer equipped with a 2400 lines/mm grating as a function of the probe delay relative to the centrifuge. An example of the experimentally detected Raman spectrogram is shown in figure 3(a). It reflects the accelerated spinning of molecules inside the centrifuge during the first 100 ps (marked by a tilted dashed white line). While spinning up, the molecules are ‘leaking’ from the centrifuge, producing a whole series of Raman sidebands—a set of horizontal lines shifted from the probe central wavelength of 398 nm. Narrow probe bandwidth enables us to resolve individual rotational states and make an easy assignment of the rotational quantum numbers to the observed spectral lines. This is demonstrated by the Raman spectrum taken at \(t = 200\) ps and shown in figure 3(b). The created wave packet consists of a large number of odd \(N\)-states, with even \(N\)’s missing due to the oxygen nuclear spin statistics. Each Raman line undergoes quasi-periodic oscillations due to the interference between the three frequency-unresolved components \(S_{1,2,3}(N)\) of the \(S(N)\) branch split by the SR interaction. An example of these SR oscillations for the \(N = 91\) Raman line is shown in figure 3(c). The oscillations start at around 100 ps, after the superrotors with the rotational angular momentum of \(91\hbar\) have escaped from the centrifuge.

The intensity of a Raman line corresponding to the transition between the states \(N\) and \(N - 2\) can be described as

\[
I_N(t) = I_0 \left| \rho_{N,N-2}(t) \right|^2 e^{-t/\tau_N},
\]

where \(I_0\) is determined by a number of time-independent parameters, such as molecular concentration and probe intensity, \(\tau_N\) is the collisional decay time constant and \(\rho_{N,N-2}(t)\) is the centrifuge induced coherence between the corresponding rotational states. As discussed above, at \(N \geq 5\), the latter consists of three main frequency components corresponding to the three \(S\) branch transitions (see figure 1),

\[
\rho_{N,N-2}(t) = \sum_{k=1,2,3} a_k e^{i\Omega_k(N)(t-t_0)},
\]

with amplitudes \(a_k\) and frequencies \(\Omega_k(N)\). Time \(t_0\) (\(0 < t_0 < 100\) ps) represents the release time of the corresponding rotational state from the centrifuge. For any \(N\), the three frequencies...
are simply \( \Omega_k(N) = [F_k(N) - F_k(N - 2)]/\hbar \), where \( F_k(N) \) are the well known spin–rotational energies of oxygen [6] and \( \hbar \) is the reduced Planck’s constant. After normalizing each measured Raman line to one at \( t = 100 \) ps (i.e. shortly after the end of the centrifuge pulse), we fit the theoretical expression to the observed signals using the following five fitting parameters \( \{a_1, a_2, a_3, t_0, \tau_N\} \). As demonstrated by a few examples in figure 4, the oscillatory behavior of our experimental data is well described by equation (1) over the whole range of angular momentum accessed by the centrifuge, from \( N = 5 \) to \( N = 109 \). Note that the weaker the line (e.g. \( N = 5 \)) the smaller the dynamic range, ultimately determined by the sensitivity of our detector.

From the fitting procedure described above, we retrieve the time constant \( \tau_N \) of the collision-induced exponential decay of rotational coherence. For the slower rotating molecules, the coherence life time is shorter than for the faster rotors. This is shown with blue circles in figure 5, where the decay rate (expressed in the units of Raman line width, \( I_N \equiv [2\pi c \tau_N]^{-1} \), with \( c \) being the speed of light in vacuum) is plotted as a function of the angular frequency of molecular rotation. Black asterisks and gray squares depict the previously reported data obtained in a thermal ensemble of oxygen molecules at room temperature (hence, \( N \leq 25 \)) using frequency-resolved [19] and time-resolved [14] detection techniques, respectively. Our results at low \( N \)’s show satisfactory agreement with both data sets. The observed decay of rotational coherence takes place on a sub-nanosecond time scale corresponding to a few collisions. Microsecond equilibration times between the rotational and translational degrees of freedom in the ensemble of centrifuged molecules have been previously reported [21].
Figure 4. The observed data (blue circles, normalized to 1 at \( t = 100 \) ps) and the fit to SR oscillations (red curves, equation 1) for six different Raman lines corresponding to the rotational quantum numbers \( N = 5, 7, 9, 21, 61 \) and 101. Experimental uncertainty (not shown) is similar to figure 3(c). Note the logarithmic scale in all panels.

Figure 5. The decay rate of rotational coherence in oxygen (blue circles, this work) and nitrogen (green triangles [17]) as a function of the frequency of molecular rotation. For convenience, rotational quantum numbers of \( \text{O}_2 \) and \( \text{N}_2 \) are shown below the frequency axis, and the decay times \( \tau_N \) are shown on the right vertical axis. Black asterisks and gray squares depict the data from [19] and [14], respectively, where the rotational decay has been studied in thermal oxygen by two different techniques. The solid red (dashed black) curve shows the result of fitting the adiabaticity correction factor \( \Omega(N) \) to the data for oxygen (nitrogen) as discussed in text.

In contrast, the coherent dynamics studied here are much faster as the superrotors are still very far from thermal equilibrium.

It has been suggested that inelastic collisions accompanied by the rotational energy transfer are the main contributors to the rotational decoherence studied in this work [24]. Hence, the
increasing coherence lifetime with increasing angular momentum is well expected from the ‘exponential-gap scaling law’ of the collisional energy transfer [25]. Slower energy transfer rates can also be anticipated from the adiabaticity argument. When the period of molecular rotation becomes comparable with, and even shorter than, the time of a single collision, molecular interactions become more adiabatic and the rotational coherence more robust with respect to collisions. The degree of adiabaticity is often expressed through the adiabaticity parameter \( a_N \) corresponding to the angle by which a molecule rotates during the collision process

\[
a_N \equiv \omega_N \tau_c = \omega_N l_c / v_c,
\]

where \( \omega_N \) is the frequency of molecular rotation, \( \tau_c \) is the collision time, \( l_c \) is the characteristic interaction length and \( v_c \) is the mean relative velocity between the collision partners. In figure 6(a), we plot the dependence of the adiabaticity parameter on the rotational quantum number of oxygen at room temperature. The adiabaticity threshold is reached at \( N \approx 65 \), where \( a_N \) crosses \( \pi \) (horizontal dashed line).

In the popular ECS scaling law [26], the adiabatic suppression of the energy transfer is taken into account by means of a correction factor \( \Omega_{l_c}(N) \),

\[
\Omega_{l_c}(N) = \left( \frac{1}{1 + a_N^2/6} \right)^2,
\]

plotted in figure 6(b). Though ECS has been very successful in describing the rotational decay of colliding \( \text{O}_2 \) molecules in the thermally accessible regime of \( a_N \lesssim 1 \) [14, 19], its applicability at higher rotational frequencies is not warranted, since the adiabaticity factor is no longer a small parameter. Yet the anticipated drop in the rate of the rotational energy transfer with increasing \( a_N \) prompted us to analyze the feasibility of describing our experimental data by means of the following simple functional form

\[
\Gamma_N = \Gamma_0 \Omega_{l_c}(N) + \Gamma_\infty.
\]

Red solid curve in figure 5 shows the result of fitting equation (5) to our data in the range of high adiabaticity (\( a_N > 1 \)) using \( \Gamma_0 \), \( \Gamma_\infty \) and \( l_c \) as fitting parameters. Good fit is achieved with the...
values \( \Gamma_0 = 76.9 \times 10^{-3} \text{ cm}^{-1} \text{ atm}^{-1}, \Gamma_{\infty} = 19.6 \times 10^{-3} \text{ cm}^{-1} \text{ atm}^{-1} \) and \( l_c = 0.56 \ \text{Å} \). The latter is close to the value found from applying the ECS model in the limit of low angular momentum \[3\], which may suggest a possibility of extending the known scaling law to the limit of high adiabaticity using the same correction factor.

It is instructive to compare these results with our recent study of rotational decoherence in centrifuged nitrogen \[17\]. Shown with green triangles in figure 5, the decay rates in nitrogen are also well described by equation (5) (dashed black curve). One noticeable difference is a lower asymptote of \( \Gamma_N \) at high \( N \)'s, reflected by the lower value of \( \Gamma_{\infty} = 2.4 \times 10^{-3} \text{ cm}^{-1} \text{ atm}^{-1} \). This may point at a non-negligible contribution of the spin-flipping collisions in the spin–rotational decoherence of magnetic \( \text{O}_2 \) molecules. The cross section for the spin relaxation of oxygen at room temperature is not known and its exact calculation is a formidable task. However, an insight can be gained from the recent studies of this process at low temperatures \[27, 28\]. As the temperature exceeds \( \approx 0.01 \text{ K} \) and approaches 1 K, the ratio between the elastic and spin-flipping collisions has been found to reach a constant of order 10, which shows little dependence on \( T \). When the temperature rises above 1 K, the energy scale of the SR splitting becomes less significant and no dramatic changes in the elastic-to-inelastic cross section ratio are expected. Given this argument, the spin-flipping cross section may indeed be somewhat below, yet comparable to, the cross section of the rotational relaxation at low \( N \) values.

Alternatively, faster decoherence of oxygen rotation may stem from the higher concentration of \( \text{O}_2 \) superrotors with respect to the concentration of the centrifuged \( \text{N}_2 \). This empirically found difference may result in the increasing local gas temperature and correspondingly higher rates of rotational energy transfer. Quantitative studies of this phenomenon are underway.

In summary, we have observed the SR dynamics in the gas of optically centrifuged oxygen molecules. Because of the interaction between the rotational magnetic moment and the electronic spin, molecules with the different spin orientation with respect to their total angular momentum rotate with a slightly different frequency. Frequency beating of the three spin components results in the SR oscillations detected in this work. Time-resolved characterization of the SR oscillations may prove useful for creating ensembles of simultaneously spatially-aligned and spin-polarized molecules. The decay of the SR coherence due to collisions has been quantified and described by means of the adiabaticity parameter.

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