Observing molecular spinning via the rotational Doppler effect

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When a wave is reflected from a moving object, its frequency is Doppler shifted¹. Similarly, when circularly polarized light is scattered from a rotating object, a rotational Doppler frequency shift may be observed²–³, with manifestations ranging from the quantum world (fluorescence spectroscopy, rotational Raman scattering and so on⁴,⁵) to satellite-based global positioning systems⁶. Here, we observe for the first time the Doppler frequency shift with a frequency shift of handedness as the incident one and a CP wave of the opposite handedness. The scattering of a circularly polarized (CP) electromagnetic wave. The scattered field consists of a CP component with the same frequency and handedness of the incident one and a CP wave propagating through a gas of synchronously spinning molecules. An ensemble of such spinning molecules was produced by double-pulse laser excitation, with the first pulse aligning the molecules and the second (linearly polarized at a 45° angle) causing a concerted unidirectional rotation of the ‘molecular propellers’⁶–⁷. We observed the resulting rotating birefringence of the gas by detecting a Doppler-shifted wave that is circularly polarized in a sense opposite to that of the incident probe.

In his famous 1905 paper on special relativity⁸, Einstein derived the frequency shift Δω for linearly polarized light of frequency ω reflected from a mirror moving with speed v and showed that in the non-relativistic limit Δω = ±2kv, where k = ω/c, c is the speed of light, and the sign depends on the relative direction of motion. When an anisotropic polarizable object rotates with angular velocity Ω, a rotational Doppler frequency shift may be observed in the scattering of a circularly polarized (CP) electromagnetic wave. The scattered field consists of a CP component with the same frequency and handedness as the incident one and a CP wave of the opposite handedness⁹–¹³ with a frequency shift of Δω = ±2Ω, where the sign depends on the relative sense of rotation. To date, table-top observations of this phenomenon have made use of mechanical rotation of anisotropic optical elements¹⁰,¹¹,¹⁴ and electro-optic effects in a nonlinear crystal subject to a rotating microwave electric field¹⁵. In the present study, we observe the rotational Doppler frequency shift (RDS) from molecules rotating unidirectionally at terahertz frequencies, which is many orders of magnitude larger than that observed in mechanically rotated systems.

We induce molecular unidirectional rotation (UDR) by applying two time-delayed, ultrashort, linearly polarized laser pulses (Fig. 1). This two-pulse technique was demonstrated by Kitano et al.⁷ and subsequently generalized¹⁶–¹⁸. Although UDR persists for as long as the molecules do not collide, the field-free anisotropy of the angular distribution gradually disappears because of angular velocity dispersion. The cigar-like shape of the angular distribution reappears periodically because of quantum revival of the rotational wave packets¹⁹–²¹ with a revival period of \( T_{rev} = 1/(2Bc) \), where \( B \) is the rotational constant. Substantial anisotropy of the angular distribution is also observed at fractions of \( T_{rev} \), especially near \( T_{rev}/2 \). Probing the ensemble at full or fractional revival enables the observation of UDR under completely field-free conditions, barring the pump from interfering with the measurements²²–²².

Let us now consider the interaction of a CP time-delayed probe pulse with an ensemble of unidirectionally rotating molecules. The polarizability anisotropy of the aligned molecules produces birefringence, which in turn converts part of the incident CP electromagnetic field into one with opposite polarization handedness. In addition, the time-varying alignment and birefringence cause a transient variation of the refractive index, which induces phase changes in the light propagating through the medium, causing spectral broadening and shifts. This phenomenon, known as molecular phase modulation (MPM), has been used previously for compression and spectral broadening of ultrashort laser pulses²³–²⁵. Finally, because of the UDR, the polarizability ellipsoid rotates with time, producing a rotational Doppler shift.

Both MPM and RDS lead to spectral changes in the probe pulse. These two effects respond differently, however, to changes in the time delay of the probe. The MPM spectral shift reverses its sign when the probe delay is scanned across the alignment (or anti-alignment) maximum. In contrast, the RDS is a one-sided spectral shift (red or blue), depending on whether the molecules and the CP probe rotate in the same or opposite directions. A full treatment of the coupled CP waves propagating in a medium with rotating birefringence is given in a forthcoming theoretical paper (by U.S., Y.P. and I.Sh.A., manuscript in preparation).

The experimental set-up is depicted in Fig. 2. A regeneratively amplified Ti:sapphire laser (peak wavelength ≈790 nm, ≈50 fs full-width at half-maximum, FWHM) was used to generate the pump and probe pulses. The three pulses intersected at the focus of an achromatic lens (f = 100 cm) in a three-dimensional...
**Figure 2 | Experimental set-up.** Pump P1 is polarized and focused by the lens into the interaction zone. The polarization axis of pump P2 is controlled by the half-wave plate (HWP). The probe is circularly polarized by polarizer $P_A$ and quarter-wave plate $QWP_A$. Polarizations are indicated by bold arrows. The delay of P2 with respect to P1 is fixed to match the alignment time. The timing of the probe pulse relative to the pumps is scanned by the motorized delay line. The circular analyser, consisting of quarter-wave plate $QWP_B$ and polarizer $P_B$, is aligned to block the probe in the absence of the pump pulses.

**Figure 3 | Experimentally observed RDS for deuterium molecules.** The peak intensity of the pump is $1 \times 10^{14}$ W cm$^{-2}$, the pulse duration is $\sim$50 fs. a–c. The spectra, shown as two-dimensional colour-coded plots, were measured with a probe scan delay of 150 fs around the midway point between the pump pulses. d–f. Normalized spectra measured at the probe delay time that produced the maximum signal (indicated by the horizontal grey lines in a–c). Vertical black line marks the central wavelength of the unperturbed probe. In a, d, only one pump is applied, resulting in no UDR and no RDS. In b, e, the molecules are set to rotate in the same sense as the CP probe, producing a redshift. In c, f, the molecules are set to rotate in the opposite sense, producing a blueshift.
Note that even for D$_2$ we cannot use the ‘impulsive approximation’, the CP probe, producing a redshift. In UDR and no RDS. Note that in (horizontal grey line in measured around the half revival times are shown as two-dimensional colour-coded plots.

Molecule (H$_2$), the alignment time under our experimental conditions is shorter than the pulse duration. We opted therefore to study deuterium molecules (D$_2$), for which the relevant timescales are longer (alignment time of $\approx$50 fs and revival time of $\approx$556 fs). Note that even for D$_2$ we cannot use the ‘impulsive approximation’, in which the pulses are assumed to be a delta function in time. Figure 3 presents three representative spectrograms, in which the transmitted probe spectrum is plotted along the horizontal axis for various probe delays (vertical axis). The spectra at the peak intensity time slice are plotted to the right of the spectrograms.

The top panels correspond to a control experiment, in which only one pump pulse was introduced, producing transient alignment but no UDR. The middle and bottom panels were recorded when the molecules were set to rotate in the same and opposite sense as the CP probe, respectively, resulting in red- and blueshifts of the transmitted light.

A second set of experiments were performed using nitrogen molecules under ambient conditions. These experiments were conducted in the open atmosphere to avoid any birefringence originating in the sample cell windows. The presence of atmospheric oxygen does not pose a problem; the larger moment of inertia of O$_2$ gives a longer revival time (11.9 ps versus 8.3 ps for N$_2$), so that the angular distribution was essentially isotropic around the time of the N$_2$ revival, when the measurements were performed.

Figure 4 depicts the RDS near the half revival time of N$_2$. As in Fig. 3, the top panels correspond to the control experiment, where only one pump pulse is present, resulting in a transient alignment but no UDR. The middle and bottom panels were recorded when the molecules were set to rotate in the same and opposite sense as the CP probe, respectively, resulting in red- and blueshifts of the transmitted light.

The magnitude of the measured RDS is consistent with a rough estimate of the unidirectional rotation frequency in the ‘molecular propeller scheme’$^{25,7}$, namely $\Delta \omega = hP/I$. Here, $I$ is the molecular...
moment of inertia, and \( P \) is the kick strength of the laser pulse\(^6\), which was \( \approx 2 \) in our experiments with nitrogen. An order-of-magnitude estimate of the frequency shift is provided in the first part of the Supplementary Information.

We performed several control experiments, which confirmed our observations. In one experiment, instead of changing the angle between the polarization axes of the two pumps with a half-wave plate, we reversed the direction of the UDR by switching the time delay between the pumps. In another, a notch filter was introduced to imprint a narrow spectral feature on the probe spectrum, and a shift of this feature was measured as a function of the probe delay. We further verified the dependence of the shift on the ‘kick strength’, and some typical data are provided in the second part of the Supplementary Information. In all cases, a clear RDS was recorded that was correlated with the sense of molecular rotation.

In conclusion, we have used coherently spinning molecules to generate a rotational Doppler shift that is six orders of magnitude greater than previously observed. To achieve this result we used a linearly polarized pulsed laser beam to align a thermal ensemble of diatomic molecules, followed by a second linearly polarized pulse to kick the molecular axes in a specified direction. The resulting unidirectionally rotating molecules were probed by a CP beam of light. Upon transmission through the spinning molecules, a part of the probe light inverted its handedness and acquired a red or blue spectral shift, depending on whether the molecules were co- or counter-rotating relative to the circular polarization of the probe.

The present work demonstrates a new approach to optical control and detection of molecular rotation. The method is intuitive; it embodies a new manifestation of the well-known rotational Doppler effect and is conceptually simple in its experimental implementation. Although we demonstrate this effect for free molecules, it is more general and may be applicable to other chiral systems, including the vectorial control of magnetization\(^7\). The molecular anisotropy induced in our scheme persists on ultrafast timescales, so that the corresponding rotational Doppler shift appears in a very narrow time window. The spatiotemporal resolution of the angular momentum anisotropy may be implemented to control ultrafast optical responses of various molecular systems and materials. The reported laser-induced RDS phenomenon may be instrumental in various fields of advanced ultrafast photonics, including vectorial polarization control and attosecond pulse generation.

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Author contributions

O.K., U.S., I.Sh.A. and Y.P. designed the experiment. O.K. performed the experiments. R.J.G. helped with the data analysis. Y.P. and I.Sh.A. provided overall guidance to the project. All authors discussed the results and contributed to the manuscript.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to Y.P.

Competing financial interests

The authors declare no competing financial interests.