

Gas-phase optical activity measurements using a compact cavity ringdown polarimeter.

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We present a compact polarimeter, which can perform sensitive measurements of optical rotation in vapor. The operation of the polarimeter is based a Cavity Ring-Down scheme which employs two signal reversals, which increase sensitivity and reduce noise, allowing the realization of sensitive measurements in the presence of spurious birefringence. We describe the operation of the polarimeter, give the basic equations for the signal analysis and retrieval of optical rotation angle, and present measurements that demonstrate a sensitivity of $\sim 80 \mu\text{deg/pass}$.

Polarimetry is a versatile technique for the measurement of optical rotation of chiral substances and is used in a wide range of fields such as biology, pharmacology, agricultural chemistry and more [1]. Most modern polarimeters operate using light whose polarization state is oscillated rapidly (usually using a Photo-elastic Modulator) and measured with a lock-in amplifier. These instruments usually measure optical rotation of chiral substances in the liquid phase with detection limits of few millidegrees. Such a sensitivity barely suffices for studying most known chiral volatile substances. For example consider the specific rotation of (R)-(+)-limonene, which is approximately $65 \frac{\text{deg}}{\text{dm}} \left(\frac{\text{g}}{\text{ml}} \right)^{-1}$ near 589 nm. A 10 cm long chamber containing (R)-(+)-Limonene at a pressure of 2 mbar (roughly the vapor pressure of limonene at room temperature) yields an optical rotation of about 0.7 millidegrees, i.e. below the detection limit of most modern polarimeters, (and at the limit of the best commercial polarimeters, with precision of about 0.3 mdeg).

Therefore, advanced optics methods are employed for studying the optical rotation of molecules in the gas phase. In general, chirality in the gas phase can be detected via a variety of methods, including femtosecond pulses [2], microwaves [3], and photo-ion imaging [4]. However, these methods are more difficult to use, and have not yet been developed commercially.

An intriguing improvement to the widely-used optical rotation method is Cavity Ring-Down Polarimetry (CRDP). The first practical implementation of such a method was introduced 20 years ago by Vaccaro and co-workers [5] and has been used to measure optical rotation values for a variety of organic molecules, in the gas phase [6,7,8,9,10,11].

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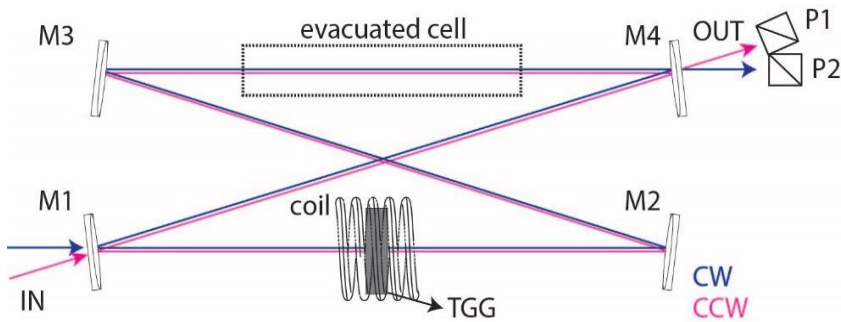


Figure 1: Drawing of the CRDP cavity set-up, showing the cavity mirrors (M1-M4), the intra-cavity TGG crystal and the coil used to produce the magnetic field, as well as the polarizers P1,2 used at the output of the cavity. Adjusted on each side of the evacuated cell are 2 anti-reflection coated windows not shown here.

In 2014, our group introduced an improved CRDP method, based on a bow-tie ring cavity, which employs two signal reversals. These can be used to increase sensitivity and allow absolute chiral measurements (without needing to remove the sample, to take a null measurement) in noisy environments. Chiral

measurements were demonstrated in the presence of noise, both in terms of variations of the refraction index (i.e. detection of open air samples), and in the presence of increased birefringence (i.e. detection via the evanescent wave produced in the total internal reflection interface of a fused silica prism) [12,13]. This Cavity Ring-Down polarimeter operated using a pulsed Ti Sapph laser system which produced ~ 32 fs, 2 mJ pulses at a wavelength of 780 nm and at a repetition rate of 1 kHz. The laser systems used for these measurements (and those by the Vaccaro group) were large and expensive, and not compatible to produce compact and relatively inexpensive polarimeters, such as those on the market. Here, we demonstrate that chiral measurements of improved sensitivity, with respect to those reported in references [12,13], can be performed by employing a low-cost microchip Nd:Yag laser, which provides 0.6 ns, 0.6 μ J at a wavelength of 532 nm and at a repetition rate of 80 kHz (Horus HLX-V-F-100). The set-up is small, and robust, and shows that a sensitive and compact polarimeter, based on CRDP, is possible.

A schematic of the polarimeter's cavity is shown in Fig.1. The cavity consists of two laser mirrors (mirrors 2 and 3, with reflectivity $R \sim 0.9997$) and two input-output couplers (mirrors 1 and 4 with $R \sim 0.998$, Layertec GmbH), and it contains an intra-cavity magneto-optic crystal. The crystal is made from Terbium Gallium Garnet (TGG), it has a Verdet constant of $\sim 200 \mu\text{rad G}^{-1} \text{cm}^{-1}$, and it has been anti-reflection coated for 532 nm to minimize reflection losses. The cavity contains an evacuated cell into which the limonene vapor is introduced. The cell is sealed with 2 anti-reflection coated fused silica windows ($R < 0.1\%$, Layertec GmbH). The linearly polarized 532 nm laser beam is injected into the cavity via mirror 1 to excite the CW cavity mode, and the reflection is retro-fed back into the cavity, again from mirror 1 to excite the CCW mode. The CW and

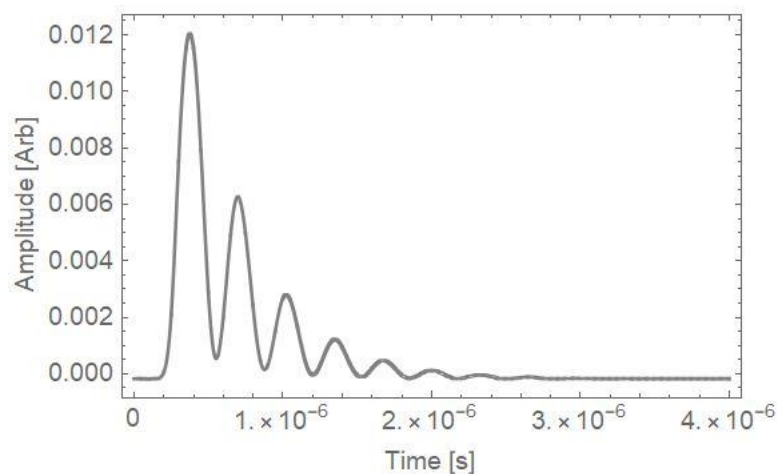


Figure 2: Experimental trace from the output of the Cavity Ring Down Polarimeter

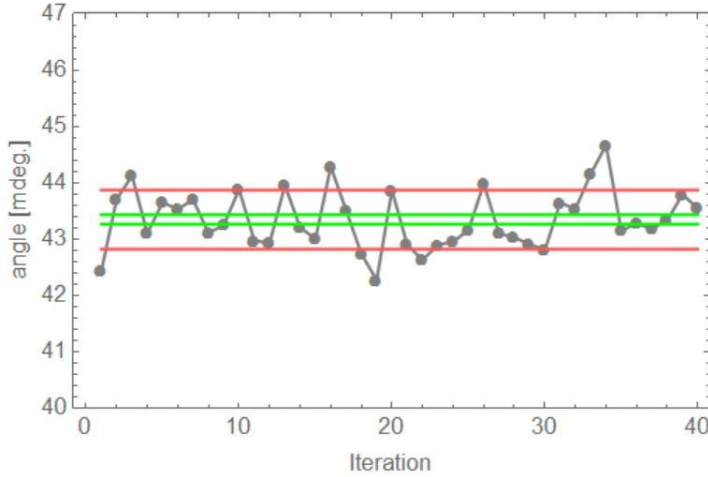


Figure 3: Measurements of the Optical Rotation angle in 1 mbar of (R)-(+)-Limonene in 40 consecutive iterations. The red lines show the standard deviation ~ 0.52 mdeg, and the green lines show the confidence interval.

is rotated by $\varphi_c + \theta_F$ where θ_F is the Faraday rotation caused by the magneto-optical effect in the TGG crystal, and φ_c is the optical rotation caused by the chirality of the sample. For the CCW mode, the polarization is rotated by $\varphi_c - \theta_F$. By reversing the direction of the magnetic field applied in the TGG crystal, the sign of the Faraday rotation is inverted for both the CW and the CCW modes. In our set-up, we employ a custom, programmable, high-power electronics board based on the Siemens TAPAS board, which permits us to invert the direction of the magnetic field at a repetition rate which can be varied between 0.5 and 100 Hz.

Since only one linear polarization component of the output light is transmitted through the polarizers P1 and P2, the output signal has the form of a damped oscillation. The exponential decay constant of this oscillation is the well-known cavity ring-down time, which for low cavity losses (typically less than 1% per pass) is equal to $\tau = \frac{nl/c}{1-R+X'}$, with n being the refractive index, l the total length of the cavity, c the speed of light, R the total mirror reflectivity and X the total losses within the cavity (such as absorption or scattering).

The frequency of the oscillation can be related to the polarization rotation inside the cavity by $\omega_{CW}(\pm B) = (\pm\theta_F + \varphi_c) c/l$ for the CW and $\omega_{CCW}(\pm B) = (\pm\theta_F - \varphi_c) c/l$. By subtracting those four frequencies according to

$$\Delta\omega(\pm B) = |\omega_{CW}(\pm B)| - |\omega_{CCW}(\pm B)| = 4\varphi_c c/l \quad (1)$$

the Faraday rotation is cancelled out and the chiral rotation is amplified by a factor of four. Most importantly, the CW and CCW modes measure the chiral sample simultaneously, therefore by subtracting the CW and CCW frequencies, the common noise cancels out, while the ability to perform the B-field inversion and the corresponding subtraction provides an additional noise-reduction mechanism.

A typical CRDP trace is shown in Figure 2. For each experimental measurement, the CW and CCW modes are recorded and the frequency of the oscillation is extracted by time-domain fitting which is performed off-line. The signals are ideally expressed by:

CCW modes simultaneously sample the TGG crystal and the chiral sample and leak out of the cavity from all four mirrors, but at a much higher rate from the two output couplers. Mirror 4 is used as an output mirror so that the cavity ring-down trace can be detected. The CW and CCW outputs are passed through two linear polarizers and are detected using photodiodes (DET36A Thorlabs) which are connected to a digital oscilloscope (Rohde & Schwarz RTO2034).

In each round trip in the cavity, the polarization of the CW mode

$$y(t) = A e^{-\frac{t}{\tau}} \cos^2(\omega t + \varphi) \quad (2)$$

where A is the signal amplitude, τ the decay time, ω the angular frequency, and ϕ is the initial phase of the oscillation. The exponential decay gives the photon lifetime in the cavity, and the oscillation gives the rotation frequency of the light pulse's linear polarization state in the cavity. The value of the angular frequency can be extracted either by Fourier analysis or by regression analysis, where the signal is fitted with a suitable model, similar to equation (2). Actual signals have a few differences from the ideal model of equation (2): Reduction in the modulation depth, may be caused by spurious linear birefringence in the cavity, or poor time resolution of the detectors. In addition, and the baseline may be not equal to zero, due to offsets introduced by the detection electronics. To account for these effects, the model is modified to:

$$y(t) = A \left(e^{-\frac{t}{\tau}} \cos^2(\omega t + \varphi) + b e^{-\frac{t}{\tau_2}} \right) + c \quad (3)$$

where now b and τ_2 are the amplitude coefficient and the decay time of the exponential introduced to account for the reduced modulation depth of the signal, and c is the voltage offset.

In Figure 3 we show the evolution of the difference frequency which is obtained after the signals are subtracted, according to (1). The mean value of this measurement is 43.34 mdeg and the standard deviation after 40 iterations is 0.52 mdeg, and the confidence interval of the measurement is 0.08 mdeg.

Measurements of chiral optical rotation of (R)-(+)-limonene, as a function of pressure in the evacuated cell, are shown in Fig. 4. The measurements reproduce the linear relation between the optical rotation and the sample pressure. The time required to obtain the data shown in Figure 4 is on the order of 5 minutes, with the main limitation coming from the inadequate data acquisition scheme: the long acquisition time is ultimately reflected on the sensitivity reported in this work.

The data acquisition is performed using a digital oscilloscope, a fact that results in roughly one in 100 measurements recorded, due to the low data transfer rate from the oscilloscope to a PC. The data acquisition can be performed in a running fashion using modern, compact electronic devices, such as Field Programmable Gate Arrays. Our group has employed such an acquisition in [14] to perform μ s-timescale, running ellipsometric measurements, where the frequency of the similar damped oscillation signals is extracted using Discrete Fourier Transform. Additional improvements to the sensitivity can result from minimizing the losses of the cavity by using mirrors with higher reflectivity and windows of higher transmission, as well as temperature stabilization and vibration isolation.

Measurements of the optical activity of (R)-(+)-Limonene have been reported in

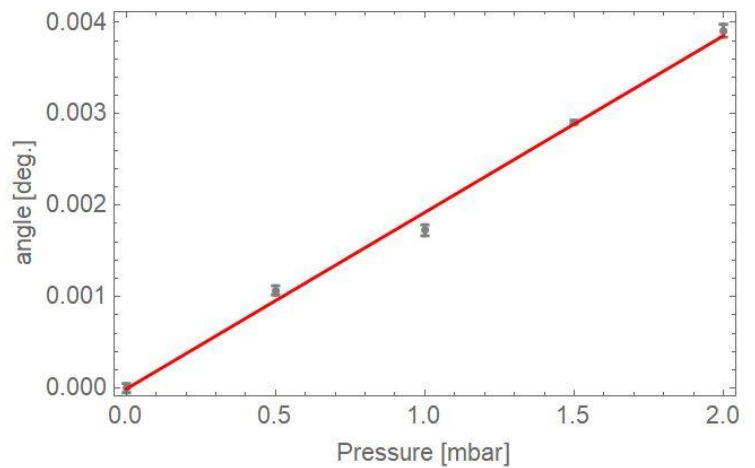


Figure 4: Measurement of the optical rotation of (R)-(+)-Limonene from 0 to 2 mbar.

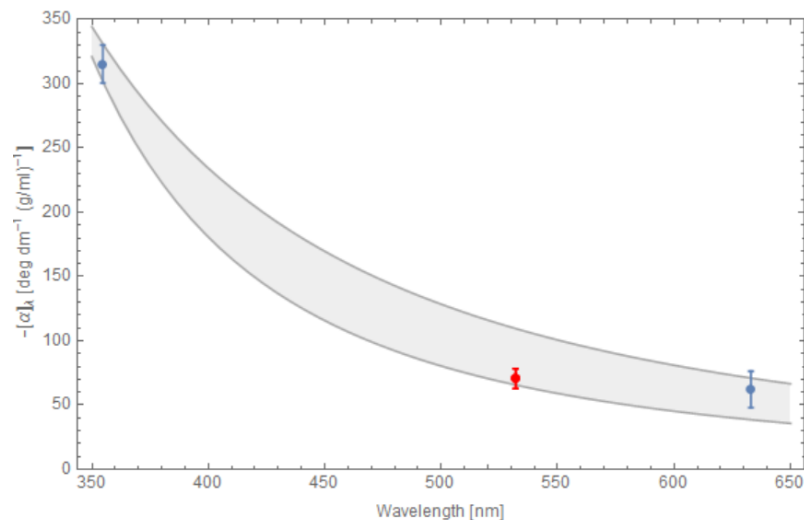


Figure 5: Evolution of the specific optical rotation of (R)-(+)-Limonene and experimental measurement at 532 nm, see text for details.

[6] both at 355 nm and at 633 nm, with the reporting specific rotation being $315.5 \pm 7.4 \frac{\text{deg}}{\text{dm}} \left(\frac{\text{g}}{\text{ml}} \right)^{-1}$ at 355 nm and $62.71 \pm 7.1 \frac{\text{deg}}{\text{dm}} \left(\frac{\text{g}}{\text{ml}} \right)^{-1}$ at 633 nm respectively. An earlier study for the specific rotation of (R)-(+)-Limonene reports a similar rotation of $304.2 \pm 11 \frac{\text{deg}}{\text{dm}} \left(\frac{\text{g}}{\text{ml}} \right)^{-1}$ [5]. Both these measurements are conducted at a temperature of 25° and are within error with respect to each other.

The specific rotation measured in a wavelength can be related to the specific rotation measured in a different wavelength according to the formula $OR(\lambda_2) = \frac{(\lambda_1 - \lambda_0)^2}{(\lambda_2 - \lambda_0)^2} OR(\lambda_1)$ [10], with λ_0 being the wavelength of the closest UV atomic transition that produces chirality. We can use the two measurements of reference [6] to extrapolate the wavelength-dependence of the optical rotation, or by using the OR measurement at 633 nm reported in [6] and the OR value reported here at 532 nm. In Fig. 5, we plot the wavelength dependence of the specific optical rotation for (R)-(+)-Limonene along the confidence interval defined by the errors in the values of the specific optical rotation reported in reference [6] for (R)-(+)-limonene at 355 nm, and the errors reported here for the specific optical rotation of limonene at 532 nm (gray curve). Together, we plot the values for the specific optical rotation reported in reference [6] for (R)-(+)-limonene at 355 nm and 633 nm, along with our measurement at 532 nm.

In conclusion, we present measurements of the optical rotation produced by low-pressure vapor of (R)-(+)-Limonene using a compact CRDP set-up, which employs a four-mirror optical cavity, a magneto-optical crystal and a low-power microchip laser and a custom, programmable electronics board, and demonstrate a sensitivity of $\sim 80 \mu\text{deg/pass}$. Furthermore, planned improvements in the data acquisition, the laser power, and temperature and vibrational isolation, will likely improve this sensitivity further.

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