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

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Received 13 February 2020
Accepted for publication 23 April 2020
Published 3 June 2020

Abstract

We present a compact polarimeter, which can perform sensitive measurements of optical rotation in vapor. The operation of the polarimeter is based on 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 \(\sim 80\ \mu\text{deg/pass}\).

Keywords: chirality, lasers, optical cavities, polarimetry

(Some figures may appear in colour only in the online journal)

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 a 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 \(65\ \text{deg dm} (\text{g ml})^{-1}\) 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 [6–11].

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.
detected by the magneto-optical effect in the TGG crystal, and the mode is rotated by $\varphi$ to a digital oscilloscope (Rohde & Schwarz RTO2034). Using photodiodes (Thorlabs DET36A) which are connected puts are passed through two linear polarizers and are detected.

The CW and CCW output of the cavity. Adjusted on each side of the evacuated cell are two anti-reflection coated windows not shown here.

In each round trip in the cavity, the polarization of the CW mode is rotated by $\varphi_c + \theta_f$, where $\theta_f$ is the Faraday rotation caused by the magneto-optical effect in the TGG crystal, and $\varphi_c$ 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 experimental 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 $\tau = \frac{\ln R}{\text{t}}$, 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 $\omega_{\text{CW}}(\pm B) = (\pm \theta_f + \varphi_c)^{\pm}/l$ for the CW and $\omega_{\text{CCW}}(\pm B) = (\pm \theta_f - \varphi_c)^{\mp}/l$. By subtracting those four frequencies according to

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

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, with a 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:

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

where $A$ is the signal amplitude, $\tau$ the decay time, $\omega$ the angular frequency, and $\varphi$ is the initial phase of the oscillation.

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 two anti-reflection coated windows not shown here.

Figure 2. Experimental trace from the output of the CRDP.
such as Field Programmable Gate Arrays. Our group has a running fashion using modern, compact electronic devices, and demonstrate a sensitivity of ~ 80 μdeg/pass.

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 [6] both at 355 nm and at 633 nm, with the reported specific rotation being $315.5 \pm 7.4 \text{ des} \left( \frac{\text{deg}}{\text{cm} \cdot \text{dm}} \right)^{-1}$ at 355 nm and $62.71 \pm 7.1 \text{ des} \left( \frac{\text{deg}}{\text{cm} \cdot \text{dm}} \right)^{-1}$ at 633 nm respectively. An earlier study for the specific rotation of (R)-(+)-Limonene reports a similar rotation of $304.2 \pm 11 \text{ des} \left( \frac{\text{deg}}{\text{cm} \cdot \text{dm}} \right)^{-1}$ [5]. Both these measurements are conducted at a temperature of 25°C 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 $\text{OR}(\lambda_2) = \frac{(\lambda_1 - \lambda_2)}{(\lambda_1 - \lambda_0)} \text{OR}(\lambda_1)$ [10], with $\lambda_0$ 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 figure 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 ~ 80 μdeg/pass. Furthermore, planned improvements in the data acquisition,
the laser power, and temperature and vibrational isolation, will likely improve this sensitivity further.

Acknowledgments

This research was partially supported by ERA-NETs co-fund action (EPOCHSE, Grant No. T3EPA-00043). This research was partially supported by ERA-NETs co-fund action. This research is co-financed by Greece and the European Union (European Social Fund-ESF) through the Operational Programme «Human Resources Development, Education and Lifelong Learning» in the context of the project ‘Reinforcement of Postdoctoral Researchers’ (MIS-5001552), implemented by the State Scholarships Foundation (IKY). We also acknowledge the European Commission Horizon 2020, ULTRACHIRAL Project (Grant No. FETOPEN-737071) for the financial support. GK acknowledges funding from the Hellenic Foundation for Research and Innovation (HFRI) and the General Secretariat for Research and Technology (GSRT), under project HANDCORE grant agreement No [1789].

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