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Absorption detection using optical waveguide cavities

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Abstract: Cavity ring-down spectroscopy is a spectroscopic method that uses a high quality optical cavity to amplify the optical loss due to the light absorption by a sample. In this presentation we highlight two applications of phase-shift cavity ring-down spectroscopy that are suited for absorption measurements in the condensed phase and make use of waveguide cavities. In the first application, a fiber loop is used as an optical cavity and the sample is introduced in a gap in the loop to allow absorption measurements of nanoliters of solution at the micromolar level. A second application involves silica microspheres as high finesse cavities. Information on the refractive index and absorption of a thin film of ethylene diamine on the surface of the microresonator is obtained simultaneously by the measurements of the wavelength shift of the cavity mode spectrum and the change in optical decay time, respectively.

Key words: cavity ring-down spectroscopy, microresonator, microsphere, fiber loop.

Résumé : La spectroscopie à cavité ring-down est une méthode spectroscopique qui utilise une cavité optique de haute qualité pour amplifier la perte optique due à l'absorption de lumière par l'échantillon. Durant cette présentation, nous mettons en évidence deux applications de la spectroscopie à cavité ring-down avec déplacement de phase qui convient aux mesures d'absorption en phase condensée et fait usage de cavités à guide d'onde. Dans la première application, une boucle de fibre est utilisée comme cavité optique et l'échantillon est introduit dans un intervalle de la boucle pour permettre des mesures d'absorption sur des nanolitres de solution au niveau micromolaire. Une seconde application est basée sur des microsphères de silice comme cavités à haute finesse. Des informations sur l'index de réfraction et l'absorption d'un film mince d'éthylène diamine sur la surface d'un micro-résonateur sont obtenues simultanément par des mesures de déplacement de longueur d'onde du spectre modal de la cavité et de changement de temps de décroissance optique, respectivement.

Mots-clés : spectroscopie à cavité ring-down, micro-résonateur, microsphère, boucle de fibre.

In the past years, absorption spectroscopy has undergone a rapid change and the absorption spectrometers that are developed in many research labs have little in common with the teaching instruments that most of us were trained on. Indeed, a typical UV–vis absorption spectrometer found in today's undergraduate labs shares many of its basic components with the “spectroscope” devised by Isaac Newton in 1666. It contains a dispersing element, such as a prism or grating, a sample compartment, and a detector that is either placed behind a slit or forms a detection array, such as a photographic plate or photodiode array. Since the experiments by Kirchhoff and Bunsen^{1,2} in the 1860s, quantitative absorption spectroscopy relies on the accurate measurement

of a change of transmitted light intensity due to wavelength-dependent attenuation by the analyte of interest. Single pass “direct” absorption detection and spectroscopy remains popular to this day, since it is straightforward to implement and many analytes show absorption features in the UV–vis region of the spectrum, whereas many solvents do not. This makes UV–vis absorption an ideal “label-free” method for detection and quantification of analytes.

On the other hand, direct absorption measurements are not background free, in contrast to fluorescence, photoacoustics, resonant ionization, coherent anti-Stokes Raman spectroscopy (CARS), and other modern spectroscopy methods. Furthermore, as evident from the Beer–Lambert law, $I/I_0 = \exp(-\epsilon C d)$,

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the sensitivity of a direct absorption measurement $dI/dC = -I_0\epsilon d \exp(-\epsilon Cd)$ depends critically on the stability of light sources, optical alignment, and detectors (all expressed through I_0).

Because of the need to measure a small intensity change on top of a large, and possibly noisy, intensity background, direct absorption is rather insensitive for low concentrations and (or) short absorption paths. Therefore, a number of approaches have been developed to overcome this limitation, notably the use of multipass cells, preconcentration of the analyte, differential absorption measurements, etc. In gas-phase spectroscopy, only a few of these methods have had an impact comparable to that of the cavity ring-down (CRD) absorption technique, a method that was introduced in 1988 by O'Keefe and Deacon.³

Cavity ring-down spectroscopy

In cavity ring-down spectroscopy, the sample is placed in an optical cavity that is usually made by opposing two highly reflective mirrors at distance d (Fig. 1). A laser light pulse that is coupled into the cavity will be trapped between the mirrors for a large number of roundtrips while its intensity decays exponentially. The characteristic decay time, or ring-down time,

$$[1] \quad \tau = \frac{t_R}{-2\ln R + \epsilon Cd}$$

depends on the pulses' round trip time, $t_R = nd/c_0$, and the reflectivity of the mirrors, R , but does not depend on the intensity of the light pulse that is coupled into the cavity or on slow fluctuations of the detector response. The ring-down time is large for high mirror reflectivity and decreases with the introduction of absorbing or scattering compounds into the cavity.^{4–6} With commercially available "super mirrors", reflectivities higher than 99.99% ($R > 0.9999$) may be achieved, which corresponds to a cavity finesse $F \approx 2\pi/(1 - R) = 62\,800$. Since this number can be roughly equated to the number of passes through the cavity medium, one can see that even a desktop cavity with length $d = 1$ m is equivalent to an absorption cell with an effective path-length of over 60 km! In addition, the sensitivity of the ring-down time measurement,

$$[2] \quad \frac{d\tau}{dC} = \frac{-\epsilon d t_R}{(-2\ln R + \epsilon Cd)^2}$$

increases quadratically with *decreasing* concentration and does not depend on intensity, which is a useful feature for an analytical spectroscopic method.

Not surprisingly, over the last twenty years, CRD spectroscopy and related cavity enhanced absorption methods have gained a larger and larger following, and the number of publications citing "cavity ring-down" in their title or abstract has increased from less than five in 1995 to over 150 in 2008. A large fraction of those publications is concerned with high resolution spectroscopy and detection of gases, of reactive intermediates, or of molecular beam-cooled samples. Since about 2002, an increasing number of research groups, including our own, attempt to adapt CRD detection to liquid samples.

CRD spectroscopy in liquids may be carried out simply by filling the entire optical cavity with liquid⁷ or by insert-

Fig. 1. (a) Mirror-based cavity ring-down scheme; (b) optical cavity consisting of two fiber Bragg gratings; (c) fiber-loop CRD showing a small gap for the sample; (d) microsphere resonator.

ing a sample cuvette^{8–10} or liquid jet¹¹ into the cavity. CRD detection for HPLC or other systems can similarly be realized by either constructing a very short cavity in which the mirrors are only separated by millimetres or by directing the effluent from the column across the optical axis of the cavity.^{12–16} Both methods achieve impressive detection limits, which are limited by their baseline noise level to about 10^{-5} to 10^{-6} absorption units, depending on the mirrors, detection wavelength, and configuration. Also, both require careful optical alignment and a trained operator. In addition, the laser pulse width needs to be shorter than the roundtrip time. This means that millimetre long cavities can only be interrogated with picosecond laser pulses and with fast data acquisition systems. An excellent review describes the implementation of the CRD detection scheme to liquids with particular emphasis on the microliter-sized samples, which are relevant for HPLC.¹²

CRD in waveguide cavities

In this presentation, we highlight two different types of optical cavities that are based on the waveguiding properties of silica and demonstrate their use for absorption measurements of small (nanoliter-sized) liquid samples.

In a simple analogy to the free-space optical cavity made of two mirrors, a strand of optical fiber that is gold coated at both end facets also acts as a high finesse optical cavity (Fig. 1b). Sigrist and co-workers^{17,18} have used such a cavity to determine the concentration of H_2 in the fiber core and to

measure bending losses occurring in the fiber optic cable. Instead of coatings applied to the fiber surface, one may also use fiber Bragg gratings (FBGs) as internal mirrors.^{19,20} FBGs are periodic modulations of the refractive index written into the core of a sensitized fiber typically using UV laser radiation. They may have a reflectivity of up to 99.99%. Light propagating along the core of the fiber is reflected from these gratings when the Bragg condition is fulfilled, i.e., when the wavelength of the light is twice as large as the grating period.

An even simpler optical cavity may be formed by connecting the two ends of a strand of optical waveguide to form a continuous loop (Fig. 1c).^{21–25} Once light is trapped inside the loop, it will circulate for many roundtrips before its intensity has decayed below the detection threshold. Compared to the linear cavity, the loop offers a number of advantages. First, the operating wavelengths are limited by the transmission spectrum of the waveguide, i.e., for silica from about 1700 nm to about 400 nm, whereas the FBGs have high reflectivity only in a 2–10 nm window, typically at around 1550 nm. Second, the gap between the fiber ends is a natural place to introduce a small liquid sample, for instance by using capillaries or channels in microfluidic devices. Third, the fiber-loop material and core diameter can be tailored to the application, whereas FBGs can be most easily written into single mode silica fibers. On the other hand, coupling light into the loop either requires couplers, which introduce cavity loss, or focusing of laser pulses onto the fiber core, which is a rather inefficient process. By contrast, FBG cavities can be simply spliced on the laser delivery fiber.

Both optical devices, the linear fiber cavity and the fiber loop, have been used in ring-down experiments. Similar to conventional free-space CRD, the ring-down time only depends on the optical loss in the cavity but is largely insensitive to lightsource power fluctuations or even detector response drifts, as long as those changes occur on timescales longer than the ring-down time. A recent review has highlighted the use of these cavities for mechanical and temperature measurements and, to a lesser extent, for refractive index measurements,²⁶ whereas we will focus on measurements of absorption induced by the interaction of the guided modes with an analyte. For a comprehensive review of cavity ring-down spectroscopic methods and in particular CRD using waveguides, the reader is directed to a 2009 book on cavity ring-down spectroscopy.⁶

CRD phase-shift measurements

Before discussing different instruments in which waveguide based CRD measurements can be used, we should emphasize the differences between absorption measurements in flow systems and the “static” gas measurements in conventional cavities.

The optical loss in a fiber loop is much higher than in even a low-finesse optical cavity consisting of mirrors. With a mirror pair of a reflectivity of 99.9%, only 0.2% of the light is lost per roundtrip, whereas the insertion loss of fiber–fiber couplers, of fiber splices, and FBGs may easily add up to more than 5%. When measuring the absorption of a sample placed between the two ends of a fiber loop, the

loss is even higher: about 10%–30% of light is lost across the gap even when it is filled with nonabsorbing solvent! For a fiber cavity having the same roundtrip time as a conventional cavity, the ring-down time is therefore much shorter and the sensitivity to changes in the optical loss due to absorption by the analyte is correspondingly lower.

Also, in the analytical separation systems discussed below, the measurement has to take place in real time, while the analyte flows between the two fiber ends, with no opportunity to average multiple “events”. The data acquisition rate has to be matched to the flow rate and the detection volume, such that the detection volume is replaced at a rate that is about 10 times slower than the acquisition rate. Practically, we need to sample a ring-down event every 1–10 ms and determine the ring-down time ($\tau = 0.1$ –10 μ s) through exponential fitting at the same rate.

In our initial experiments, we used pulsed dye lasers operating at about 800 nm and were restricted in our data acquisition rate by the 10–100 Hz pulse repetition rate of our lasers.^{21,22} Also, we had to average about 2000–6000 ring-down events to obtain a reliable ring-down time. The resulting data acquisition rate of 1/3 min^{−1} to 1/10 min^{−1} (one measurement every 3–10 min) is grossly inadequate for analytical flow measurements. While the rate can be increased considerably by switching to kHz repetition rate lasers, the main problem remains: the duty cycle of the experiment is woefully low. Assuming a 10 kHz repetition rate, light that is injected in the cavity rings down (in about 10 μ s) only for a small fraction of the time, while the remaining time the system does nothing (90 μ s). Finally, it is neither trivial nor cheap to switch inexpensive lasers or other light sources, such as LEDs, on nanosecond timescales, and it is also costly to read out ring-down transients at high sampling rates.

All three concerns, the fast ring-down times, the poor duty cycle, and the high cost of (sub-)nanosecond switching and readout, may be addressed by applying a simple method that has been used in fluorescence lifetime measurements for many decades. Instead of monitoring the decay of a pulse in the time domain, one can also monitor the phase shift of an amplitude-modulated signal in the frequency domain (Fig. 2).^{27,28} If an intensity-modulated signal is continuously fed into a high finesse cavity (or a fluorescent sample), the cavity (or sample) will emit light at the same modulation frequency, ω , but with reduced modulation depth and with a phase shift that depends on the ring-down time, τ (fluorescence lifetime). For a single exponential decay, the phase shift is^{28,29}

$$[3] \quad \tan(\phi - \phi_0) = -\omega\tau$$

Here, ϕ is the phase shift between the light entering and exiting the fiber cavity and ϕ_0 is the phase shift resulting from instrumental factors such as electronic time constants and propagation delays. For multiexponential decays, the relation is more complicated but one can still determine the ring-down times and the relative amplitudes of each exponential component from phase-angle measurements at multiple modulation frequencies.³⁰

The point is, phase-shift CRD measurements, introduced for spectral analysis by Engeln et al. in 1996,³¹ are ideally

Fig. 2. Similar to a RC circuit, the response of an optical cavity is different to an impulse (DC, top) or an oscillating input (AC, bottom). An optical cavity, which is driven with a sinusoidally modulated input of angular frequency, ω , will emit light with the same modulation frequency but reduced modulation depth and phase shifted to the input.

suited for transient absorption detection in low finesse optical cavities.³² Phase-shift CRD is compatible with short ring-down times, since the modulation frequency may be set to the inverse of ring-down times. Changes in ring-down time as low as a few nanoseconds and picoseconds are readily measurable. Also, the duty cycle of the phase-shift measurement is unity, i.e., there is always light in the cavity. The readout rate is limited only by the ring-down time; “on the fly” exponential fitting is no longer required. Finally, phase comparators are also comparably inexpensive; simple integrated circuits with a 1° resolution may be bought for a few dollars.

Unfortunately, the ring-down times calculated from phase angles are sensitive to scattered light and are also less accurate compared to an exponential fit to a 10 000 point decay trace. Nevertheless, for our applications, the advantages, especially regarding data acquisition rate and cost, outweigh the disadvantages, and in all setups described below, the phase-shift CRD method was employed.

Fiber-loop ring-down absorption detection

In a 2006 article, we presented three different interfaces between the fiber loop and the flow systems.³³ In one device, a commercial microcross was used to achieve fair coupling of light between the two ends of the fiber loop, which were fixed at a distance of 5–50 μm from each other.³⁴ Two capillaries were inserted orthogonal to the optical fibers and used to flow samples of cyanine dyes in water between the fiber ends (Fig. 3). A detection limit of 200 $\mu\text{mol/L}$ corresponded to a minimal detectable absorption loss, α_{min} , $< 50 \text{ cm}^{-1}$. The flow rate of 10 $\mu\text{L/min}$ and injection

Fig. 3. Three interfaces of the fiber loop with a fluidic system. Left: a microfluidic chip into which the fiber loop is inserted; right top: a commercial microcross with the fiber ends and capillary ends inserted normal to each other; right bottom: a 300 μm capillary through which a hole was drilled to insert the two fiber ends. The fiber ends have hemispherical lenses at their ends.

volume of 2 μL are compatible with capillary electrophoresis or micro-HPLC, but unfortunately, the limit of detection (LOD) is too large to be competitive with existing detection methods. Because it is difficult to optimize the optical alignment of the fibers in a microcross and thereby increase the sensitivity, we decided to use a second approach.

A 360 μm capillary (ID: 100 μm) was embedded in a block of polymethyl methacrylate (PMMA) and a 150 μm hole was drilled through the block and normal to the long axis of the capillary (Fig. 3, right bottom). The fiber ends were inserted to be flush with the inside wall of the capillary and about 60 μm apart and then fixed using epoxy glue. The LOD was improved over the microcross to 50 $\mu\text{mol/L}$ ($\alpha_{\text{min}} = 10 \text{ cm}^{-1}$). The detection limit and sensitivity could be further improved by using hemispherical fiber ends instead of flat fiber end faces. This dramatically increases the coupling efficiency across the sample gap from 60% to about 90%.³³ To create hemispherical lenses, we heated the fiber ends in the electric arc of a fusion splicer.³⁵ The fiber ends were then inserted as before and placed 30 μm apart before being glued in place. Using lensed fiber ends, the LOD was improved to 10 $\mu\text{mol/L}$ ($\alpha_{\text{min}} = 1.6 \text{ cm}^{-1}$) and protein detection became feasible.

A third interface was created to a microfluidic chip made of glass. Again, the flow channel was first sealed and encapsulated in PMMA and then a 150 μm hole was drilled mechanically perpendicular to the channel. The flat-cut fiber ends were inserted and fixed at a distance of 14 μm . The LOD of 30 $\mu\text{mol/L}$ ($\alpha_{\text{min}} < 10 \text{ cm}^{-1}$) was respectable, especially considering the short absorption path and the small detection volume of 700 pL. Note that the absolute quantity of detected analyte was only 21 fmol at the detection limit.³³

All experiments above were conducted at 800 nm, i.e., a wavelength that was matched to the absorption maximum of the cyanine dye. At this wavelength, the fiber optic loss is quite low (3 dB/km) and the photomultiplier tubes used to detect scattered light from the loop show high sensitivity. Of course, a practical absorption detector for capillary elec-

trophoresis, microfluidics, or micro-HPLC needs to work at much shorter wavelengths. Because standard fiber optic cables have much reduced transmission at wavelengths shorter than 500 nm, it was believed that fiber-loop ring-down detection is not feasible at the important blue and UV wavelengths.

With recent advances in UV fiber optic materials, fiber CRD detection has now become possible, and in a recent publication we demonstrated the quantification of tartrazine dye, of myoglobin protein, and of a proprietary pharmaceutical ingredient using phase-shift fiber-loop ring-down detection at 405 nm.³⁶ The experiment was possible because of the low loss of the UV fiber optic loop ($\alpha = 0.011 \text{ cm}^{-1}$) and of a specially designed fiber-optic–fluid interface (shown in Fig. 4), that combined a small detection volume (6 nL) with an even smaller dead volume (estimated at <2 nL). At the same interface, light from the 405 nm laser diode was introduced using a power delivery fiber that irradiated the gap between the fiber ends and thereby allowed for scattered blue light to enter the loop (Fig. 4). Despite the fact that the fiber ends were not lensed and comparatively far apart (190 μm), the detection limit is improved to 1 $\mu\text{mol/L}$ for myoglobin (Fig. 5) and the minimum detectable absorption loss is lower compared to our best earlier interface by almost an order of magnitude ($\alpha_{\text{min}} = 0.11 \text{ cm}^{-1}$). This is likely due to the improved alignment between the fiber ends and the larger fiber core diameter, both leading to lower optical losses across the sample gap. More importantly, it is likely that the same setup will perform well at even shorter detection wavelengths and we plan to couple light from a 255 nm LED into the fiber loop in the near future.

With the interface displayed in Fig. 4, the detection of single micron-sized particles is also possible. The Mie scattering cross section increases with decreasing scattering wavelength and even the detection of transparent particles is possible if their refractive index differs by more than about 0.15 from the solvent. Indeed, we were able to detect single polystyrene particles of 5 μm diameter that were suspended in water using a detergent (Fig. 5). Since these particles are comparable in size and refractive index to *Escherichia coli* cells, we expect that cytometry and single cell pathogen detection should be feasible using this very inexpensive and compact setup. Earlier experiments with an interface that was far from optimized and the 810 nm detection wavelength were conducted, and showed detection of yeast cells and *E. coli* cells, but not, yet, at the single cell level.³⁷

Microsphere ring-down absorption detection

While the fiber loop is a “long roundtrip/low finesse” optical cavity, microresonators are optical cavities with very high finesse and extremely short roundtrip paths of typically less than a millimetre.^{38–41} Microsphere resonators (shown schematically in Fig. 1d) have been used as chemical sensors for many years.^{42–52} Light can be coupled tangentially into such a sphere, such that it travels along the “equator”. This so-called “whispering gallery mode (WGM)” can only be excited if the circumference of the sphere is an integer multiple of the excitation wavelength, and if the mode field

Fig. 4. Computer rendering of the optical–fluidic interface. The delivery fiber in the foreground illuminates the fiber gap. Capillaries attached to the top and bottom plate feed sample solution through small holes in front of the delivery fiber and out through a hole in the bottom plate.

Fig. 5. Detection of transparent 5 μm diameter polystyrene particles (top trace) and detection of myoglobin in buffer solution at 405 nm (bottom) using the interface shown in Fig. 4.

of the whispering gallery mode overlaps with the mode field of the delivery waveguide. A whispering gallery mode can remain localized near the equator of the sphere for a very long time; in an analogy to the acoustic equivalent in the “whispering gallery” of, say, St. Paul’s Cathedral in London. Much like the sound of a whispered voice is guided along the inside of the Cathedral’s dome, light remains guided by total internal reflection. Light may be coupled into the sphere using, for example, tapered fibers (as we have done),⁵³ evanescent-field access blocks, angled fiber ends, or regular prisms.⁴⁰

Refractive index measurements of analytes adsorbed on such microresonators are comparatively straightforward WGM frequency measurements. Since microresonators are very short, high-finesse cavities; they exhibit a sharp cavity mode spectrum, which depends strongly on the roundtrip length of the whispering gallery modes. The frequency of each WGM is, of course, influenced by the size of the microsphere, i.e., the circumference at the equator, but also by temperature and the refractive index of the immediate environment of the sphere. A thin layer of analyte adsorbed on the surface will effectively increase the circumference of the sphere. Of course, such an adsorbate may also attenuate the WGM intensity and reduce the number of roundtrips that one WGM experiences. Both quantities, the refractive index of the environment and its optical absorption, can therefore be obtained *simultaneously* from the frequency shift of the cavity fringes, and from their associated ring-down time, respectively.⁵⁴ Below, we intend to illustrate that such combined absorption and refractive index measurements using silica microsphere resonators are sensitive, but also quite simple.

In separate setups, silica resonators have already demonstrated superb performance for the measurements of both the refractive index and the optical absorption of adsorbed analytes. For example, researchers have used a toroidal microresonator to demonstrate the detection of a single interleukin-2 molecule through a combination of the induced refractive index change and optical absorption of the adsorbed molecule leading to heating and expansion of the sphere, the so-called thermoptic effect.⁵² Simultaneous absorption and refractive index measurements of a few monolayers of an adsorbed species are easily feasible.⁵⁵ On the other hand, compared to the thermo-optic effect, cavity ring-down experiments provide a more direct measure of the optical absorption of an adsorbed layer but have, to our knowledge, not yet been used in chemical measurements. They were used, however, in characterizing the optical loss in microresonators. For example, Vahala and co-workers⁵⁶ conducted the CRD measurement in the time domain and obtained ring-down times of 43 ns for a 90 μm diameter microresonator. The submicrosecond ring-down time highlights the fact that the roundtrip path for such devices is typically less than one millimetre and only about 280 μm in this particular case. It is probably because of the short ring-down times, even for microresonators having a high finesse, that they have been used almost exclusively for refractive index measurements but not for absorption measurements.

On the other hand, a “large” square quartz monolith (7.5 mm $\times$ 7.5 mm $\times$ 5 mm) has been used as a high finesse cavity by Pipino⁵⁷ in 1999 and CRD absorption detec-

tion of 0.006% of a monolayer of I_2 on the quartz surface was realized. Ring-down times of over a microsecond gave a finesse of over 12 500!

The finesse of the 300 μm diameter silica microsphere cavities used in our group is between $F = 5\,000$ – $100\,000$ and the ring-down times are correspondingly on the order of 4–70 ns, meaning that they will have to be measured with a resolution of picoseconds.

As in the fiber loop experiments, measurements of fast ring-down events at a high duty cycle may be achieved cost efficiently and simply through phase-shift CRD. By setting the modulation frequency, $\omega = 1/\tau$, we achieve optimal sensitivity to phase angle changes irrespective of the finesse or ring-down time of the cavity. While their appearance is very different, these microresonators show very similar behaviour compared to “regular” ring-down cavities consisting of two or more mirrors and to the above fiber-loop cavities. For example, in all three types of cavities the overall cavity loss depends on the losses inside the cavity medium *and* the losses that occur when light is coupled in and out of the cavity. The whispering gallery mode can interact with the sample through its evanescent field, i.e., the small part of the mode field that is located *outside* the sphere and decays exponentially over the distance of only a few 100 nm.

Recently, our group has demonstrated phase-shift CRD measurements on a 300 μm microsphere and determined the attenuation that a WGM experiences.⁵⁸ In the following, we briefly describe the optical setup and highlight the theoretical and analytical aspects of this work.

The silica microspheres were formed by fusing the end of a single-mode optical fiber (Corning, single mode fiber, SMF-28) to obtain a sphere with a nominal diameter of about 300 μm . The residual optical fiber stem allows for manipulation and positioning of the microsphere. A tapered single-mode optical fiber, with a waist diameter of about 3–4 μm , was used to couple light into the evanescent field of the microsphere WGM (Figs. 1 and 6). A detailed description of the experimental setup regarding the microsphere and tapered waveguide may be found elsewhere.⁵³

Two different lasers were used. A tunable diode laser (Ando AQ 4320D, power: 3 mW) with a linewidth of about 200 MHz was used to optimize the coupling into the sphere and conduct proof-of-concept measurements of the phase angle associated with ring-down events on selected WGMs. An Er-doped fiber-ring DFB laser (Koheras Adjustik E15, linewidth < 1 kHz, power: 100 mW) was employed to interrogate the microsphere when ethylene diamine was deposited onto its surface.

The laser output was sinusoidally intensity modulated using a Mach–Zehnder modulator (JDS Uniphase) up to a modulation frequency of 2 MHz. A polarization controller, positioned after the modulator, allowed the TE and TM resonator modes to be selectively excited, although we were not able to distinguish between these two polarization states. Rayleigh back-scattering from imperfections in the silica microsphere quickly equilibrates degenerate counter-propagating cavity modes.⁵⁹ In our previously published work, WGM resonances were observed as dips in the delivery fiber transmission spectrum and as intensity peaks in the scattering spectrum from the microsphere. We also derived expressions (valid for angular modulation frequencies, ω ,

Fig. 6. Scheme of the setup used for phase-shift CRD spectroscopy of microsphere resonators.

that are much lower than the carrier frequency) for the phase shifts that can be observed by recording the intensity modulated signal of the light transmitted through the fiber taper, and of the light scattered from the sphere.

$$[4] \quad \Delta\phi_{\text{trans}} \approx -\frac{2\omega n_{\text{eff}}L}{c} \frac{2\ln(\Gamma)}{(\ln\Gamma)^2 - (\alpha L/2)^2}$$

$$\Delta\phi_{\text{scatter}} \approx -\frac{2\omega n_{\text{eff}}L}{c} \frac{1}{-2\ln\Gamma + \alpha L}$$

Clearly, the two phase angles have a different dependence on the optical coupling, Γ , between the fiber and the resonator and the optical loss, αL , of the WGM. Since both phase angles may be recorded simultaneously, we can obtain values for both Γ and αL for each WGM. As for “regular” cavities, it is possible to transfer nearly all the power into the cavity, i.e., at “critical coupling”. This condition is achieved, here, when $\Gamma_{\text{critical}} = 0.9998$ and $\alpha_{\text{critical}} = 0.43 \text{ m}^{-1}$. At this point, the phase angle of the transmitted light is infinite, and the intensity carried by the fiber taper drops to zero. Phase-angle measurements of the transmitted light are therefore biased to detect WGMs near critical coupling, whereas for scattered light, WGM with the lowest total loss ($-\ln\Gamma + \alpha L$) show the largest phase angles.

With $-\ln\Gamma$ and αL one can easily calculate the nominal ring-down time

$$[5] \quad \tau = \frac{n_{\text{eff}}L}{c(-\ln\Gamma^2 + \alpha L)}$$

For the four WGMs that were investigated, we obtained $\tau = 4 \text{ ns}$ to 8 ns , corresponding to quality factors (Q factors) of the order of 10^6 – 10^7 . Most importantly for chemical detection, the attenuation term, α , will change when an analyte is adsorbed to the microresonator surface and absorbs (or scatters) the WGM.

While the scattered light in previous work was collected through a microscope lens placed above the sphere, we also recorded WGM resonances that were detected through Rayleigh backscattered light. Conveniently, the Rayleigh

backscattered counterpropagating modes are partly coupled back into the delivery waveguide. A fiber optic circulator, positioned before the polarization controller, extracted the backscattered light and directed it to a fiber-coupled, 6 GHz bandwidth InGaAs detector (Thorlabs, Inc. SIR5). A radio-frequency lock-in amplifier (Stanford Research Systems Model SR844) processed the detector output, providing, simultaneously, an intensity and a phase-angle measurement that was referenced to the laser modulation. As the narrow band-width laser was slowly scanned, the lock-in amplifier’s outputs of intensity and phase shift were recorded. The entire optical setup was placed under a Plexiglas™ enclosure and purged with dry nitrogen to reduce contamination. Dry nitrogen was also used to sweep ethylene diamine (Sigma-Aldrich, used without purification) vapour from a flask into the plastic enclosure, with a partial pressure of about 10 Torr. Once a suitable shift in the WGM resonance was observed, the dosing was stopped and the chamber sealed. Ethylene diamine could be removed from the microsphere by purging the chamber with a continuous flow of dry nitrogen.

The presence of ethylene diamine in the vicinity of the silica microsphere surface manifests itself in two ways: through a shift in the cavity resonance position to longer wavelength and through a reduction in the optical lifetime (ring-down time) of the mode. Experimental results are shown in Figs. 7 and 8. The reduction of the ring-down time is also responsible for the decreased amplitude and larger linewidth in the phase-shift spectrum (Fig. 7). The magnitude of the phase shift has been measured for a number of modulation frequencies.

Previously, it has been shown that ethylene diamine adsorbs strongly to silica through interactions with surface silanol groups.⁶⁰ We assume, in our case, that the observed perturbations of the cavity resonance are due to adsorbed ethylene diamine, rather than vapour, by virtue of the method by which the compound was introduced. This assumption was confirmed in, as yet, unpublished calculations.

Arnold et al.⁴³ have derived an expression describing the wavelength shift of a WGM due to molecules adsorbed on a

Fig. 7. Redshift of the whispering gallery mode resonance at $1.56\ \mu\text{m}$ (dashed red line) upon adsorption of ethylene diamine on the microsphere resonator (solid black). The phase shift was recorded at a modulation frequency of $\omega = 3.77 \times 10^6\ \text{rad/s}$.

Fig. 8. Phase shift of the Rayleigh backscattered light from the microsphere resonator as a function of modulation frequency measured with respect to the forward propagating modes. Due to the increased loss upon adsorption of ethylene diamine (black squares), the ring-down time, i.e., the slope, decreases.

microsphere surface. In our experiment, the observed shift of the WGM resonance upon dosing the microsphere with adsorbate was $12.8 \pm 0.2\ \text{pm}$ from which a coverage of about 3 monolayers may be estimated using the polarizability of bulk ethylene diamine. Since water vapour is ubiquitous and is also strongly adsorbed on silica, the measured surface concentration of ethylene diamine also indicates that water has been displaced by ethylene diamine.

The surface coverage can also be obtained from the absorption measurement, i.e., from the decrease in phase shift (ring-down time) as the ethylene diamine concentration increases. For a single exponential decay, the phase shift of the intensity-modulated light is related to the ring-down time, τ , by eq. [3]. From Fig. 8, the ring-down times with and without ethylene diamine present are $\tau = 68 \pm 7\ \text{ns}$ and $\tau_0 = 44 \pm 4\ \text{ns}$, respectively. Note that this WGM has much lower loss compared to the WGM described previously by

our group.⁵⁸ From the ring-down times and using an estimate of the fraction of the evanescent field that can interact with the adsorbed layer, it is possible to again estimate the surface coverage of ethylene diamine as about seven monolayers using the absorption coefficient of bulk ethylene diamine (EDA).

The discrepancy of the value obtained through phase-shift CRD absorption, three monolayers ($\Sigma_{\text{EDA}} = 3.6 \times 10^{15}\ \text{cm}^2$) with the value of seven monolayers ($\Sigma_{\text{EDA}} = 1.5 \times 10^{15}\ \text{cm}^2$) that was obtained using the wavelength shift of the same WGM may be attributed to either a decrease of the ethylene diamine polarizability and (or) an increase of the absorption cross section of ethylene diamine compared to the bulk liquid. This is not surprising as it is well-known that the mid-infrared absorption cross section of ethylene diamine at silica surfaces is markedly higher than that of the bulk liquid.⁶⁰ Also, the alignment of the surface complex is normal to the sphere surface and is expected to cause further deviations of the absorption cross section and polarizability from the bulk liquid ethylene diamine values, both of which were obtained in isotropic samples.

In any case, it is possible to estimate the detection limit for the phase-shift CRD microsphere resonator detector. For our particular setup and WGM, we can measure a 10% change of the ring-down time (corresponding to best-fit errors of Fig. 8), and can therefore detect a surface coverage of $\Sigma_{\text{EDA}} = 6.5 \times 10^{14}\ \text{cm}^2$ corresponding to less than 1.5 monolayers.

Future work will focus on improving this detection limit by using lasers with narrower line widths. Also, a careful survey of the WGM spectrum may yield better suitable WGM with higher Q factors. Finally, we require independent measurements of the surface refractive index and absorption of ethylene diamine to quantify the surface concentration with higher accuracy. Similar measurements should also be possible at different wavelengths, e.g., in the visible region of the spectrum or even in the mid-infrared region given the availability of narrow band lasers and waveguide materials.

While microsphere resonators are well-suited for the optical characterization of thin films, it would be much more difficult to use the optical cavity itself as a tool for chemical identification. Overtone absorption and refractive index of the film are both “broad band” spectroscopic features that carry little information on the exact identity of the chemical composition of the film. Chemical (bio-) detection of targeted molecules is possible, however, by functionalizing the surface such that the analyte of interest adsorbs and then interacts with the optical cavity.

Conclusions

With this presentation, we intended to show the potential and limitations of two rather exotic applications of absorption spectroscopy. We concentrated this discourse on simple absorption measurements, but it is easily demonstrated that the fiber-loop ring-down method also has other applications, such as the measurements of refractive indices,⁶¹ of loss in fiber optic components, of strain, temperature and pressure.^{62–64} Here, the sensitivity of fiber optic devices such as

fiber Bragg gratings and long-period gratings to environmental parameters may be exploited.

Similarly, one can functionalize the surface of microspheres to obtain selectivity to analytes of interest. Refractive index measurements combined with thermoptic response of the cavity have already led to the detection of a single interleukin-2 molecule on silica microtoroid resonator.^{52,55} Direct absorption measurements on functionalized spheres have not yet been conducted but are certainly in the realm of phase-shift CRD.

While it appears that CRD absorption measurements using waveguide loops or microresonators are only of limited use for measurements of trace gas concentrations (the strength of mirror-based CRD spectroscopy), and of “large liquid volume” absorption spectroscopy (the strength of direct absorption), the methods may evolve into a useful tool for the measurements of the absorption of small liquid volume and small amounts of adsorbed substances.

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