PERSPECTIVE

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Innovations in cavity ringdown spectroscopy

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Cavity ringdown spectroscopy, based on the decay of light intensity within a high finesse optical cavity, is one of the most sensitive and versatile spectroscopic absorption techniques currently available. This Perspective examines some of the growing number of novel variations on the standard technique and evaluates their potential applications in spectroscopy and chemical/biological sensing.

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1. Introduction

Cavity ringdown spectroscopy (CRDS) has its origins in technology developed by the aerospace industry for characterising high reflectivity mirrors.[1,2] Its application to molecular absorption measurements was first described by O'Keefe and Deacon in 1988,[3] and over the past ten years or so it has become established as the ultra-sensitive spectroscopic detection technique of choice for a wide variety of applications, ranging from fundamental studies of molecular spectroscopy, kinetics and dynamics through to atmospheric and environmental sensing. A literature search using a popular citations database reveals an almost linear growth in publications in the field over the past decade, from around 10 per year in 1994 to over 100 in 2004.

The basis of all cavity ringdown techniques is a measurement of the decay of light within a high finesse optical cavity. In most applications, the cavity is formed from a pair of high-quality plano-concave mirrors (see Fig. 1), often having reflectivities greater than 0.9999. In the most straightforward version of the technique, a pulse of laser light is directed into the back face of one of the mirrors, and the small amount of light coupled through the mirror into the cavity is repeatedly reflected backwards and forwards between the two mirrors. On each reflection, a small amount of light is lost (mainly due to transmission/absorption by the mirrors or absorption by gases inside the cavity), with the result that the amount of light within the cavity decays exponentially with time. The exponential decay is recorded by positioning a sensitive photodetector behind the second mirror to detect the tiny amount of light leaking out of the cavity through the mirror on each pass. The time constant τ of the decay is given by:

$$\tau = \frac{d}{c(L+\alpha l)} \qquad (1)$$

where d is the cavity length, c the speed of light, L the cavity loss in the absence of a sample (equal to $1 - R$ for a simple two-mirror cavity, where R is the mirror reflectivity), and α the absorption coefficient of an absorbing species present over a path length l within the cavity. As eqn. (1) shows, apart from details of the experimental setup, such as the length of the cavity and the reflectivity of the mirrors, the only parameter the exponential decay constant depends upon is the absorption coefficient of the gas in the cavity. An absorbing gas added to the cavity will lead to greater losses on each pass, and therefore a shorter time constant for the exponential decay. If the laser wavelength is scanned, the exponential decay time constant recorded at each wavelength may be transformed into an absorption coefficient, yielding the absorption spectrum of the gas in the cavity. Because the measured decay constant is independent of the absolute intensity of light injected into the cavity, CRDS has the distinct advantage over single pass techniques that it is largely insensitive to noise caused by shot-to-shot fluctuations in the intensity of the pulsed laser source. The absorption coefficient α may be related to the photo-absorption cross section σ and the number density n of the species of interest by $\alpha = \sigma n$. Detection sensitivities for particular gases are dependent on their photo-absorption cross section at the wavelength of interest, but are routinely in the parts-per-million to parts-per-billion range. The sensitivity of the technique increases in line with the mirror reflectivity R, since this determines the loss per cycle ($L = 1 - R$), and therefore the overall path length through the sample. However, in pulsed cavity ringdown, increasing the sensitivity in this way

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Fig. 1 Schematic of a cavity ringdown spectrometer (see text for explanation). A stable cavity is obtained by employing plano-concave mirrors with a radius of curvature chosen to re-focus the light on each reflection.

reduces the overall signal levels due to the reduced amount of light coupled through the cavity to the photodetector on each pass. For many applications, this particular problem may be overcome using 'CW' techniques, in which light is accumulated in the cavity to detectable levels over a significant time period (several ringdown time constants), following which the light source is switched off and the ringdown decay measured.[4,5] In this configuration, the ringdown time constant may also be determined from a measurement of the 'build-up' time of the light in the cavity to a steady state intensity. A variant on this approach is the phase-shift cavity ringdown technique,[6] in which the ringdown time, and therefore the absorption spectrum, is extracted from a measurement of the magnitude of the phase shift experienced by an intensity-modulated CW beam injected into the cavity. The phase shift θ is related to the ringdown time τ by $\tan\theta = -\omega\tau$, where ω is the modulation frequency of the light source. A true CW variation on the CRDS technique is cavity enhanced absorption spectroscopy (CEAS).[7,8] This is based on the premise that under continuous illumination at a wavelength resonant with one of the cavity modes, the total light intensity that builds up inside a cavity is to a good approximation proportional to the ringdown time. An absorption spectrum may therefore be obtained from the wavelength dependence of the total time-integrated intensity leaving the cavity. It should be noted that since CEAS involves the measurement of absolute intensities rather than decay rates, the technique is again susceptible to fluctuations in laser power over time.

CRDS experiments of the type described above provide a straightforward approach to making high sensitivity measurements of absorption spectra or number densities, predominantly for gas-phase species. While such applications still account for the majority of CRDS measurements, in recent years, the introduction of a number of variations on the standard two-mirror CRDS experiment has broadened the scope of cavity ringdown measurements considerably. The aim of this Perspective article is to explore some of these novel applications of the cavity ringdown technique and to evaluate the potential of the emerging technologies. For an overview of conventional CRDS applications, the reader is directed towards a number of excellent reviews.[8–13]

2. Broadband CRDS—multiplexed and two dimensional techniques

Most single pass absorption spectrometers employ a broadband light source in order to make simultaneous measurements at all wavelengths in the spectral region of interest. The polychromatic light transmitted through the sample and through an empty reference cell is dispersed in space, and the ratio of the two signals at each wavelength is converted to an absorbance to yield the spectrum. This approach provides fast data acquisition times and high signal to noise ratios, though the relatively short path length means that the absolute detection sensitivity is considerably lower than in ringdown methods. In contrast, when making a ringdown measurement, considerable care is usually taken to ensure that the laser bandwidth is significantly smaller than the width of the absorption line(s) under study. If this were not the case then the losses in the cavity due to the absorber would vary over the range of wavelengths present, and the measured signal would be a multi-exponential function, complicating the data analysis. Most CRDS measurements employ a tuneable monochromatic laser source, which is scanned over the wavelength region of interest. In this way, absorbances are measured one wavelength at a time, and data acquisition rates are correspondingly slow.

There have been a number of reports in the literature in which broadband radiation sources have been used in cavity ringdown measurements, many of which are described in a recent review article.[11] However, in most cases a monochromator is used to scan the wavelength either at the entrance to or exit from the cavity, so that the actual ringdown measurements are not broadband and there is no improvement in data acquisition time. One technique of this type that perhaps deserves mention is the Fourier transform CRDS approach developed by Engeln and Meijer,[14] in which the broadband output of the cavity is passed through an interferometer capable of making time-resolved measurements on the timescale of a ringdown transient. The measured interferogram is a function of both the optical path length difference between the two arms of the interferometer, and of time, and Fourier transformation yields ringdown traces for each frequency interval. In principle, such an approach would allow broadband ringdown spectra to be measured in a matter of seconds; however, in practice, the 50 Hz repetition rate of the broadband dye laser source used resulted in a measurement time of nearly 4 hours for an interferogram consisting of 3260 discrete mirror positions, each summed over 200 laser shots. A phase shift version of the technique has also been developed.[15]

Another approach to broadband ringdown measurements, suggested by Czyzewski,[16] is to disperse the broadband light through a spectrograph as it leaves the cavity and image the resulting pattern at a fixed time using a gated CCD (charge-coupled device) camera. By sweeping the gate of the CCD through the ringdown decay over consecutive laser pulses, the broadband ringdown decay trace may be obtained. While the broadband character of the source is retained in the ringdown measurement, this method suffers from the fact that because the time dependence of the ringdown trace is acquired over several laser shots, the insensitivity to laser shot noise, one of the great strengths of CRD measurements, is lost. There have only been a very few cases in which both the absorbed wavelength and the ringdown decay are measured simultaneously, allowing a complete spectrum to be obtained with each laser shot. Two different, but related, approaches have been described, both of which involve spatial wavelength dispersion of the light as it exits the cavity.

The first approach was developed by Scherer,[17,18] and is known as ringdown spectral photography. A gratingless dye laser was used as the broadband source. Broadband radiation leaving the cavity is incident first on a rotating mirror, and then on a diffraction grating, before being directed onto a two-dimensional CCD detector array, as shown in Fig. 2a. The rotating mirror disperses the beam in time, with radiation leaving the cavity at different times striking different points on the diffraction grating, and the diffraction grating disperses it in wavelength along an axis perpendicular to the time axis. This

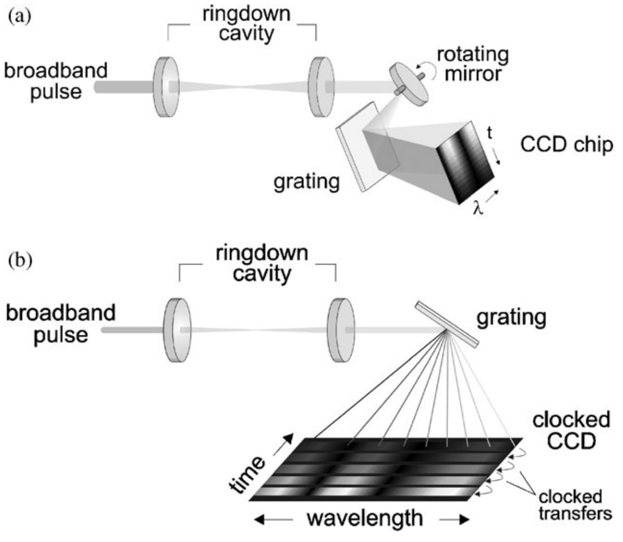

Fig. 2 Experimental setup for: (a) ringdown spectral photography; (b) clocked-CCD broadband CRDS. See text for details.

yields a two-dimensional image on the detector with time along one axis and wavelength along the second. The grating and CCD pixel resolution used allowed a spectral resolution of around 1.5 cm^{-1}, sufficient to study rotational structure. The temporal resolution is determined by the rotation speed of the mirror and by the pixel resolution of the CCD, but was typically around 40 ns per pixel under the conditions chosen. The technique has been demonstrated through measurements on propane and on the $b^1\Sigma_g^+ \leftarrow X^3\Sigma_g^-$ ($\nu'' = 1,0$) system of oxygen.

In the second technique, developed by Ball *et al.*,[11,19] a spectrograph is used to disperse the broadband light leaving the cavity onto a horizontal region of a two dimensional *clocked* CCD array. The clocked CCD transfers the image captured on a given row of pixels down to the next row on the CCD chip once every 0.5 μs, leaving the original row ready to acquire a new image (see Fig. 2b). The illuminated region may therefore capture a series of one-dimensional 'snapshots' of the wavelength-dispersed images of the cavity output at a series of fixed times (determined by the clocked transfer time) within the ringdown decay. The complete two-dimensional image built up in this way contains wavelength information along the horizontal axis and time information on the vertical axis, in much the same way as the ringdown spectral photography technique described above, with an overall time resolution of around 5 μs. This technique was also demonstrated through measurements on the $b^1\Sigma_g^+$ ($\nu' = 1,2$) $\leftarrow X^3\Sigma_g^-$ ($\nu'' = 0$) transitions of molecular oxygen[11] and has also been applied to detection of the NO_3 radical.[19]

3. Polarisation-dependent cavity ringdown

Spectroscopic measurements made with unpolarised light yield the absorption coefficient of the sample as a function of wavelength, and are usually employed either to obtain structural information on the absorbing species, or to determine the quantity present in a given sample. By analysing the polarisation of the light entering and leaving a ringdown cavity, it is possible to obtain additional information on optical rotation and polarisation-dependent absorption. Engeln *et al.*[20] first used this approach in 1997, combining CRDS measurements with magnetic polarisation spectroscopy. The system they used to demonstrate the new technique was the $^PP_1(1)$ line of the now-familiar $b^1\Sigma_g^+$ ($\nu' = 1,2$) $\leftarrow X^3\Sigma_g^-$ ($\nu'' = 0$) magnetic dipole transition in molecular oxygen. In the presence of a magnetic field, the lower state splits into three Zeeman components with $M_J = 0, \pm1$. The $M_J = 0$ component is only able to absorb light polarised perpendicular to the applied magnetic field, with the $M_J = \pm1$ components absorbing light polarised parallel to the field. This polarisation-dependent absorption leads to an effective rotation of the plane of polarisation known as magnetic dichroism, which may be measured by splitting the light emerging from the cavity into its two orthogonal polarisation components. In addition, the plane of polarisation may rotate due to magnetic circular birefringence, when different polarisation components have different velocities through the sample (otherwise known as rotary dispersion). By making measurements with the applied magnetic field both parallel and perpendicular to the axis of the ringdown cavity, it is possible to separate these two effects. Engeln *et al.* demonstrated a significant improvement in sensitivity over previous methods used to measure these effects; they were able to measure polarisation rotations as low as 10^{-8} rad cm^{-1} and differential absorptions of $\sim 3 \times 10^{-9}$ cm^{-1}. The technique was also shown to be applicable to the study of magneto-optical rotation in transparent solid samples.[20]

Though the work of Engeln *et al.* was directed towards studying magneto-optical effects in gaseous and solid samples, it is notable that the sensitivities attained are sufficient to probe optical rotation arising from intrinsic molecular chirality. Such measurements are complicated by the fact that, unlike magneto-optically induced effects, the symmetry properties of chirality-induced polarization phenomena would lead to cancellation of any observable optical rotation effect on each round trip of the cavity using the scheme described above. Vaccaro and coworkers[21,22] overcame this problem with the development of a technique known as cavity ringdown polarimetry (CRDP). As shown in Fig. 3, the method relies on the incorporation into the cavity of a pair of $\lambda/4$ plates with their axes slightly offset from one another. Circularly polarised light is injected into the cavity, and the combination of $\lambda/4$ plates and cavity end-mirrors causes the plane of polarisation of the linearly polarised light present between the two $\lambda/4$ plates to rotate slightly on each round trip of the cavity. The circularly polarised light leaking out of the cavity is converted back to linearly polarised light using another $\lambda/4$ plate, and is detected through a linear polariser. The resulting signal consists of an exponential ringdown decay, upon which is superimposed a series of fast oscillations caused by the rotation of the (linear) polarisation during the ringdown pulse. A chiral sample introduced into the cavity induces an additional rotation, modifying the frequency of the fast oscillations and providing a probe of the optical activity of the sample. Cavity ringdown polarimetry has proved to be an extremely sensitive probe of both circular birefringence (nonresonant rotary dispersion) and circular dichroism (resonant differential absorption) in chiral samples, to the point where measurements may be made on low pressure gases rather than the usual liquid samples. This allows a direct comparison to be made with the results of *ab initio* calculations, and also allows measured optical activities of isolated gas-phase molecules to be compared with their solution phase counterparts. Measurements on samples of α-pinene, β-pinene, *cis*-pinane, limonene, fenchone and propylene oxide revealed significant differences between the gas and solution phase values, and allowed the intrinsic optical activity of the molecules to be separated from solvent-mediated effects.

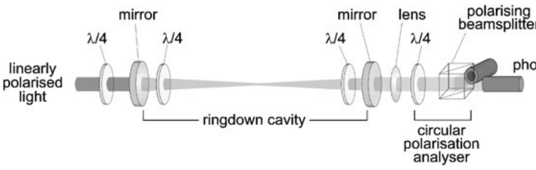

Fig. 3 Experimental setup for cavity ringdown polarimetry.

4. Fast timescale kinetics

In common with other types of absorption spectroscopy, CRDS has been widely used in kinetics studies, though almost exclusively to investigate processes occurring over a timescale considerably longer than the ringdown time constant (see for example ref. 23). Under these conditions, the density of the absorbing species remains approximately constant during each ringdown trace, such that the traces may still be treated as pure exponential functions. When the process under study occurs on a timescale similar to the ringdown constant, the changing concentration of the absorber during the ringdown pulse will produce a decay that is no longer a simple single exponential decay. Even so, when a time-varying absorption coefficient $\alpha(t)$ is incorporated into the data analysis, time-resolved CRD measurements of this type provide a highly sensitive probe for fast-timescale kinetic processes, with the further advantage that a complete kinetic measurement may be made on each laser shot. Given the relative simplicity of the technique, and its potential applications to highly reactive transient intermediates and/or kinetics measurements in unstable environments, it is perhaps surprising that there have been only a few reports of its use to date.

The first documented example was provided by Brown *et al.*[24] In addition to deriving detailed expressions for the

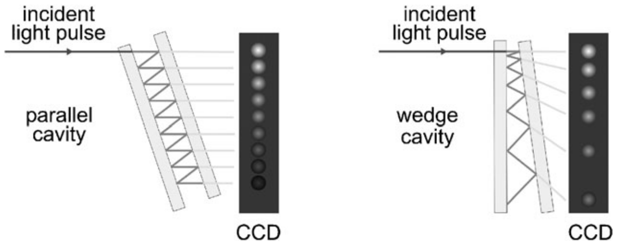

Fig. 4 Cavity walkoff spectroscopy using a planar and a wedge-shaped cavity.

intensity decay within the cavity for a number of different kinetic schemes, they measured rate constants for the reactions $NO + NO_3 \rightarrow 2NO_2$ and $OH + HNO_3 \rightarrow H_2O + NO_3$ at 296 K, in both cases detecting the NO_3 radical, and obtained rate constants that matched literature values to within the measurement uncertainty. In another application, Yalin *et al.*[25] successfully used the technique to monitor the concentration of N_2^+ ions within a pulsed atmospheric-pressure nitrogen plasma, backing up their CRDS measurements through comparison with electrical conductivity measurements on the plasma.

It is also possible to extend time-resolved cavity ringdown measurements into the picosecond regime through the use of femtosecond laser pulses, ultrashort cavities and ingenious detection schemes. In 'bounce by bounce' cavity ringdown,[26] Zare and coworkers inject an 87 fs pulse from a Ti-Sapphire laser into a 139 μm long cavity with a round-trip time of between 600 and 1000 fs. Since the laser pulse width is significantly shorter than the cavity round trip time, the ringdown signal consists of a series of pulses with an exponentially decaying envelope. In order to sidestep the problem of finding detectors with a sufficiently fast time response to quantify these signals, the pulse train leaving the cavity is passed through a time microscope,[27] which expands the pulse train in time by a factor of 100 to the point where individual pulses may be measured in time by a commercially available detection system. The data is analysed by comparing the intensities of consecutive pulses, rather than by fitting the entire ringdown decay (the relative intensities of consecutive pulses are related in a straightforward way to the instantaneous ringdown time constant of the cavity), allowing the sample concentration to be probed with a time resolution on the order of the round trip time of the cavity. The viability of the technique was demonstrated by making measurements firstly on an empty cavity, and then with the cavity filled with either ethanol or an organic dye dissolved in ethanol.

In a new variation on the 'bounce by bounce' ringdown method, Zare and coworkers have designed a variety of cavities in which consecutive pulses experience a 'walkoff' from the cavity axis,[28] as shown in Fig. 4. The spatially separated output pulses from the cavity are then detected by a CCD camera. Knowledge of the cavity geometry allows the spatial separation of the pulses to be transformed directly back into a temporal separation to reconstruct the ringdown train as a function of time. The walkoff effect may be achieved either by directing the laser pulse into a plane-mirror cavity in an off-axis direction, or by directing it on-axis into a wedge-shaped cavity, in which one of the mirrors is tilted relative to the other. A temporal resolution of better than 4ps is attainable using this technique.

5. Measurements on condensed phase samples in two-mirror cavities

Though cavity ringdown spectroscopy is fast becoming the technique of choice for making sensitive absorption measurements on gaseous samples, high absorption and scattering losses in condensed-phase samples mean that the ringdown time is usually too short for standard two-mirror CRDS techniques to be effective. The most straightforward way to make measurements on liquid samples is to place the solution inside the cavity in direct contact with the mirrors, in much the same way as for a gaseous sample. However, due to the considerations outlined above, there have only been one or two studies in which this approach has been taken. Hallock *et al.*[29] showed that by choosing the solvent carefully to minimise background absorption and scattering, ringdown times of several hundred nanoseconds could be obtained through a solution in contact with the cavity mirrors in a 21 cm long cavity. This corresponds to a detection limit of 10^{-6} cm^{-1}. Though this is a very respectable value, it is much lower than is possible for a gas phase sample, and restrictions on the optical properties of the solvent are likely to limit the applications of this approach. In particular, common solvents such as water, methanol and ethanol show too much background absorption to be used at the wavelengths studied. Despite this caveat, in a later kinetic study on the reduction of Methylene Blue,[30] the authors were able to use their technique to follow concentration changes on a microsecond timescale for species present in solution at the parts-per-billion to parts-per-trillion level.

The first liquid phase CRD measurements were carried out by Xu *et al.*,[31] and employed either one or two sample cells inserted into the cavity at Brewster's angle, minimising reflection losses when light of the appropriate polarisation was used to excite the cavity. The use of a separate sample cell within the cavity also allowed a large enough mirror separation to obtain reasonable ringdown times of around 1 μs without suffering unduly large scattering and absorption losses in the liquid. Xu measured spectra of the fifth vibrational overtones of the C–H stretch in benzene, both for the pure liquid and for a solution of benzene in hexane, and showed a detection sensitivity sufficient to measure absorption coefficients as small as 2–5 × 10^{-7} cm^{-1}. The Brewster cell approach has been adopted in a number of subsequent experiments. For example, Zare and coworkers[32] have designed a Brewster's angle flow cell that allows CRDS to be used as a detection technique for high performance liquid chromatography. In the first application of CRDS for fast-timescale kinetic measurements of photo-induced reactions in solution, Alexander[33] has determined second order rate coefficients for reaction of NO_3 with a series of terpenes.

Similar approaches have also been used to study thin films and monolayers, usually by coating the substance of interest onto a transparent substrate which is then inserted into the cavity. Meijer and coworkers[34] made measurements on 20–30 nm thick films of C_{60} by coating it onto a ZnSe substrate placed inside the cavity. The substrate was aligned perpendicular to the light propagation direction such that all of the various 'embedded' cavities were optically stable. While time consuming, this ensured that light reflected from surfaces within the cavity was returned to the cavity rather than contributing to the overall cavity loss. The experiments used tunable infrared light near 8.5 μm from a free electron laser, and achieved monolayer sensitivity in the measurement of one of the fundamental IR absorption lines of C_{60}. The technique has been used more recently by Logunov[35] to study thin films of poly(methyl methacrylate) at wavelengths of 1.3–1.5 μm, and by Vaschenko *et al.*[36] to make measurements on SiO_2 and Ta_2O_5 films on a silica substrate. Muir and Alexander[37] made the first thin film measurements in the visible, examining the structures of thin films of oxazine and malachite green dyes coated onto borosilicate substrates. In their case polarised laser light was used to excite the cavity, and the substrate was inserted at Brewster's angle to minimize reflections, rather than aligned to return reflections to the cavity. Sub-monolayers of oxazine with coverages as low as 0.032 were observed, with an absorption loss per pass of 5.79 × 10^{-5}. The spectra also showed evidence for the formation of dimers and higher aggregates on the borosilicate surface. Brewster angle cavity ringdown spectroscopy has also been carried out on C_{60} films in the infrared by Marcus and Schwettman.[38]

Instead of placing the thin film of interest onto a coated plate between the cavity mirrors, it is also possible to use the mirrors themselves as a substrate. This approach was taken by Kleine *et al.*[39] in their measurements on iodine in the region from 16 200–17 200 cm^{-1}. While the absence of extra optical elements within the cavity reduced scattering losses by a factor of ~100, coating the mirrors directly is only feasible for measurements on substances that will not cause irreversible damage to the dielectric mirror coatings.

All of the condensed-phase measurements described so far involve direct passage through the sample of the light trapped within the cavity. An alternative is to set up the cavity so that the sample absorbs an evanescent wave emitted from a surface at which the trapped light undergoes total internal reflection. Because the evanescent wave propagates only a very short distance (on the order of a wavelength) from the interface, such a configuration is ideal for investigating surface processes. Such an application was first described by Pipino *et al.*[40] in 1997. Pipino incorporated a Pellin–Broca prism into a two-mirror cavity (see Fig. 5a) and demonstrated sub-monolayer detection of I_2 *via* evanescent wave absorption at the prism surface. Pipino remarked on the simplicity of the scheme for studying surface processes compared with other methods such as electron spectroscopies and non-linear optical techniques. A similar approach was adopted by Shaw *et al.* in their work on the pH dependence of adsorption at a silica–water interface.[41,42] In these experiments, the sample of interest is coated onto a Dove prism placed in the centre of a two-mirror cavity (see Fig. 5b), and absorbs the evanescent wave emitted at the point where the laser beam totally internally reflects from the prism surface. The presence of the prism in the cavity reduces the ringdown time from around 15 μs to 150–200 ns, which was sufficient to measure absolute absorbances of order 10^{-4}. Using this technique, Shaw *et al.*[41] studied adsorption of crystal violet ions to a charged silica surface as a function of pH in high ionic strength solutions of NaCl, KCl and $CaCl_2$. They observed an increase in absorption with increasing pH, and found evidence for competitive binding between the crystal violet and metal cations. In a later study carried out on a Nile blue derivative using the same technique,[42] it was shown that evanescent wave cavity ringdown may be used to monitor interfacial pH with a resolution on the order of 0.001 pH units.

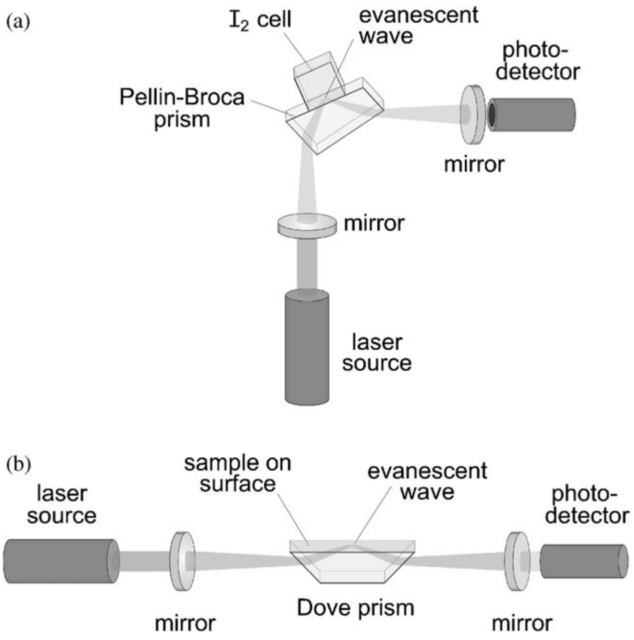

Fig. 5 Evanescent wave CRD using total internal reflection at the surface of: (a) a Pellin–Broca prism; and (b) a Dove prism.

6. Cavities based on total internal reflection phenomena

In addition to incorporating total internal reflection phenomena into a two-mirror cavity, there has also been considerable recent interest in developing ringdown cavities based entirely on total internal reflection. The dielectric mirrors used in two-mirror cavities are expensive, and generally only work over a fairly narrow range of wavelengths, typically between ten and a few tens of nanometres. Cavities based on total internal reflection have the advantage that they are effective over a broad range of wavelengths, and are also often well suited for making measurements on both gas phase and condensed phase samples. In addition, polarisation and reflection losses inherent in the hybrid cavities described previously are often largely eliminated.

Pipino extended his work on evanescent wave cavity ringdown by designing a monolithic total-internal-reflection-ring minicavity.[43–45] The cavity, shown in Fig. 6, consists of an optical cube with a single convex face, which refocuses the internally circulating light to form a stable optical resonator. Light is coupled into and out of the cavity by photon tunnelling through a pair of coupling prisms. For a cavity with a 2.12 cm round trip path length, ringdown times on the order of 1 μs are possible, yielding sensitivities of $\alpha_{min} = 10^{-7}$ to 10^{-6} cm^{-1}. An additional feature of the minicavity is that it will propagate both in-plane (p) and out of plane (s) polarisation modes, allowing the polarisation dependence of the absorption to be monitored. In measurements on I_2 adsorbed to the resonator surface,[44,45] the differential absorption of s and p polarisations, together with the orientation of the transition dipole for the probed transition, indicates that the I_2 molecules lie flat on the surface rather than adsorbing ‘end-on’. Pipino also speculates that by optimising the optical material and size of the minicavity, and choosing an appropriate wavelength region, it may be possible to achieve single molecule detection with such a resonator for a wide range of chemical species.

One of the best-known applications of total internal reflection is optical fibre technology, and it is perhaps not surprising that there is currently a great deal of interest in fibre-based variants of cavity ringdown spectroscopy. von Lerber and Sigrist[46] formed a linear fibre cavity by depositing a high reflectivity coating ($R > 0.999$) onto both ends of a length of optical fibre. Such a cavity is essentially identical to a standard two-mirror cavity, with the exception that rather than placing the sample inside the cavity, the species of interest absorbs the evanescent wave present near the surface of the fibre core. Bending an optical fibre causes a small amount of light to be coupled out from the core to the fibre cladding, and as a test of the experimental setup, the loss from the core, measured *via* the reduction in ringdown time constant, was matched to the manufacturer’s specifications for a range of bend radii. The authors also demonstrated evanescent wave absorption of

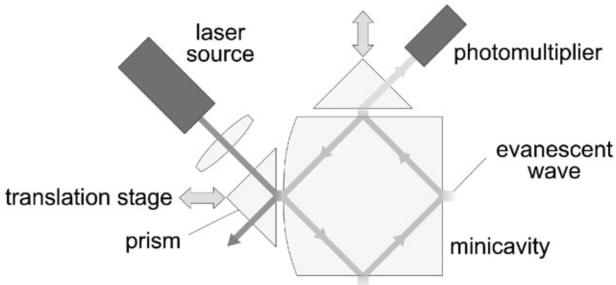

Fig. 6 Miniature resonator based on total internal reflection for evanescent wave cavity ringdown.

the guided core mode by observing a steady reduction in ringdown time as the fibre cladding diameter was decreased by etching in a solution of buffered hydrofluoric acid. There is also one example in which a dielectric coated fibre is used to measure absorption spectra of compounds present *within* the fibre. Vogler *et al.*[47] used such a cavity to monitor hydrogen diffusion into and out of optical fibres. Diffusion of H_2 into optical fibres, and subsequent reactions that form optically absorbing species within the fibre, is thought to be one of the primary processes responsible for degradation of fibre transmission characteristics over time.

An alternative method of producing high finesse fibre cavities is to employ fibre Bragg gratings (FBGs). These are produced by irradiating a photosensitive fibre with a UV laser beam to change the refractive index of the fibre core in a periodic pattern. The grating is permanently imprinted on the fibre core, and is designed to reflect a predetermined range of incident wavelengths. FBGs have several advantages over mirror-coated fibre ends, namely that they are insensitive to the quality of the fibre end polish, and the reflection is always normal to the fibre axis. Gupta *et al.*[48] were able to produce a variety of cavities of this type using different production techniques, with losses ranging from 0.2% to 2.3%, largely attributable to absorption by compounds produced within the fibre during the grating fabrication process. Spectroscopic measurements on solutions of glycerin in water were made by immersing a section of fibre from which the cladding had been partially stripped to expose the evanescent wave from the fibre core.

One of the most recent and promising developments is fibre-loop ringdown spectroscopy, based on circulation of light within a closed loop of optical fibre. In contrast to CRDS experiments involving dielectric mirrors or fibre Bragg gratings, the range of wavelengths that may be utilised in a fibre-loop spectrometer is limited only by the transmission characteristics of the fibre, and may cover several hundred nanometres (this is also true of the total-internal-reflection minicavity described previously). The most straightforward implementation of fibre-loop CRDS, shown in Fig. 7, is that of Loock and coworkers.[49–51] The fibre loop is formed from a length of multimode fibre whose ends are joined by a commercial mechanical splice connector. Light from a pulsed dye laser is coupled into the loop through side illumination of a bent section of fibre, and further around the loop, a small amount of light is coupled out through another bend to a photomultiplier. The ringdown trace obtained is found to be a bi-exponential, due to light coupled into the fibre core and cladding having different decay rates (900 and 235 ns respectively for a 12 m length of fibre). To record a spectrum, a tiny volume of sample is placed between the fibre ends. With a fibre end separation of 3.8 μm, giving a total illuminated volume of $\sim 7.4 \times 10^{-12}$ L, spectra were recorded for solutions of the dye 1,1′-diethyl-4,4′-dicarbocyanine iodide (DDCI) in DMSO as a function of concentration. Both the recorded spectra and the concentration dependence of the absorption were in good agreement with the expected curves. Loock and coworkers have also demonstrated phase-shift fibre-loop ringdown spectroscopy,[52] a direct analogue of the phase-shift cavity ringdown technique first developed by Engeln *et al.* and described in the Introduction. During the course of this work, a detailed characterisation of the various loss processes affecting the ringdown time was carried out. These include intrinsic losses associated with the optical fibre and connector, mechanical strain (bending of the fibre), and lateral and longitudinal displacement of the fibre ends.[50] The significant effect that mechanical strain has on the ringdown time constant within a fibre loop cavity has since been exploited by a number of groups in the development of highly sensitive strain gauges[53] and pressure sensors.[54,55]

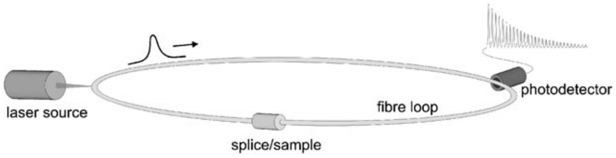

Fig. 7 Fibre loop ringdown spectroscopy.

Stewart and coworkers,[56–58] the first group to report fibre-loop ringdown measurements, are developing techniques based on infrared fibre lasers with the aim of probing vibrational overtone bands of molecules such as CO, CO_2, C_2H_2, H_2S, NH_3, OH, H_2O and HI. The experimental setup is constructed from commercially available fibre-optic components manufactured for the telecommunications industry, including couplers to couple light into and out of the loop, a tuneable bandpass filter and variable attenuator, and a micro-optic sample cell constructed from gradient refractive index lenses. The sample cell alone introduces a loss of around 20% per pass, and further smaller losses are introduced by the other components, such that the overall losses around the loop as it stands are far too large for useful ringdown measurements to be made. Stewart and coworkers resolve this problem by incorporating an erbium doped fibre amplifier (EDFA) into the loop. The amplifier gain may be tuned to offset losses around the loop as desired, making it possible in principle to obtain arbitrarily long ringdown times and hence extremely high sensitivities to absorbing species placed in the sample cell. This is a truly inspired idea, and in theory could lead to orders-of-magnitude improvements in detection sensitivity. However, its success hinges on the ability to achieve stable gain close to, but just below, the lasing threshold for the EDFA. This requires the amplifier to be both highly linear, so that gain remains constant during the ringdown trace as the absolute light intensity decays, and also highly stable between laser pulses, so that the ringdown time for successive traces is the same. Unfortunately, this has proved problematic, and though the situation has been improved through the incorporation of additional gain stabilization stages into the loop, it has not yet been possible to stabilize the amplification to the point where spectroscopic measurements have become feasible.

Lehmann and coworkers[59] have also demonstrated fibre-loop ringdown spectroscopy in the telecommunications region of 1530 nm, in both pulsed and continuous wave (CW) mode (see Introduction). Light is coupled into and out of the loop by means of a pair of 99 : 1 fibre couplers, which are readily available at this wavelength. The couplers are fusion spliced into the loop to minimise losses, allowing a completely closed loop to be formed, with no mechanically spliced ends. Instead of placing the sample between the fibre ends, the sensing region consists of a tapered region of fibre that promotes evanescent field absorption by the sample. Evanescent wave absorption in the resulting cavity was demonstrated by recording a spectrum of 1-octyne over the wavelength range from 1525–1550 nm, which agreed well with the corresponding spectrum measured on an FTIR spectrometer. It should be noted that evanescent wave absorption is typically only around 0.1% as sensitive as direct absorption, though this may be offset somewhat by the longer ‘empty cavity’ ringdown time (and therefore greater sensitivity) achievable when there is no physical break in the fibre loop. Very recently, Lehmann’s group have used the same experimental scheme to detect single cells adsorbed to the surface of the fibre taper sensing region.[60] The tapered region was chemically treated with poly-D-lysine, to which the cells bind. Bound cells scatter the evanescent wave emitted from the fibre taper, increasing the loss associated with the fibre loop and decreasing the ringdown time. The ‘empty cavity’ ringdown time was measured to be 73.4 μs, with each adhered cell reducing the ringdown time by around 0.23 μs. In addition, the change in ringdown time was linear over the range from 0 to 150 adsorbed cells. In the future, by coating the fibre taper with binding agents specific to chosen cell lines, this intriguing application of cavity ringdown spectroscopy has the potential to provide highly sensitive single-species biosensing of a range of cells, and possibly even viruses and proteins. In common with all absorption spectroscopies, CRDS is not specific to the analyte of interest: all species present with non-zero absorption coefficients at the chosen irradiation wavelength contribute to the total measured absorption signal. In a wider context than the biological examples considered above, fibre tapers could be chemically modified for specific binding of a range of chemical species, providing exciting possibilities for a wide range of highly sensitive, highly specific sensors.

7. Future directions

The frontiers of cavity ringdown spectroscopy have advanced considerably since its original incarnation as a simple, highly sensitive technique for making spectroscopic absorption measurements on gaseous samples. In recent years, the technique has been modified and expanded to the point where current CRDS techniques allow measurements to be made on gases, liquids and solutions, thin films, and even solids, with time resolutions ranging from seconds down to femtoseconds. While cavity ringdown is already widely used in kinetics studies, the high sensitivity and time-resolution offered is likely to lead to it being used increasingly as a detection scheme for dynamics experiments, in both gaseous and condensed phases. For gas phase measurements, CRDS should offer a highly sensitive detection method for species that are difficult to detect using traditional high-sensitivity detection schemes, such as laser-induced fluorescence (LIF) and resonance-enhanced multiphoton ionization (REMPI).

Future advances are likely to lead to even higher sensitivities, possibly even approaching single molecule sensitivities, novel cavity geometries, and a host of new applications. Fibre-loop techniques, for example, hold obvious potential for biosensing or lab-on-a-chip applications. Cavities based on total internal reflection may often be made considerably more compact and rugged than traditional two-mirror cavities, making them suitable for a range of atmospheric and environmental sensing applications. A promising direction that has only just begun to be explored is the use of microcavities based on total internal reflection. Ringdown traces have already been measured for 'whispering gallery modes' circulating near the surface of glass microspheres and similar structures;[61–63] Armani *et al.*[63] recently recorded a 43 ns ringdown within a tiny, 100 μm 'microtorus', and 30 ns ringdowns have been recorded in small microspheres.[61] While ringdown decays in microcavities of this type have not yet been used directly for spectroscopic measurements (though there have been indirect applications—see for example ref. 64), such devices may eventually provide a diverse range of miniature sensors for a variety of applications.

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