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Walk-off ring-down spectroscopy: attaining ultrafast resolution by converting time into space

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A new technique for monitoring time-resolved phenomena is demonstrated by which a probe beam is directed into an optical cavity. Spatially separated output pulses are produced by directing the incident beam into the cavity in such a way that it walks in a direction transverse to the optical axis as it propagates between the two mirrors. This effect may be achieved either by a plane-parallel resonator oriented at a nonzero angle of incidence or by a wedge cavity, for which one of the mirrors is set at an angular offset. The spatially resolved output train may then be related to the time-dependent attributes of the resonator and the molecules it encloses. Time resolution is controlled by the separation of the mirrors, wedge geometry, and the angle of incidence. A time resolution of better than 4 ps is achieved using a 500 μm mirror separation and a 20° angle of incidence.

1. Introduction

Time-resolved measurements of ultrafast phenomena are of interest to chemists in a broad spectrum of sub-fields, including solvation, electron transfer, isomerization, relaxation, and unimolecular decay. This information may be obtained indirectly from high-resolution spectroscopic studies in the frequency domain [1] or by direct temporal measurement. This article concerns the latter type of experiments in which the dominant method for studying such phenomena is pump–probe spectroscopy. In this technique, the time delay between the excitation source and the monitoring signal is varied to determine how the optical properties of the chemical system of interest change with time [2, 3]. The fundamental principle of pump–probe experiments has been incorporated into a wealth of techniques, including direct absorption spectroscopy [4], coherent anti-Stokes Raman spectroscopy (CARS) [5], photon echo spectroscopy [6], transient grating optical Kerr effect [2], and thermal lens spectroscopy [7]. Although the basic pump–probe methodology is ubiquitous, it is unable to monitor continuously the consequences of a single pump event because every pump–probe delay represents an independent measurement. Consequently, the technique cannot be used to measure molecular properties that are strongly dependent upon the pump event but may not be reproducible from one event to the next, such as laser ablation or laser plasma generation. We report an alternative procedure that can measure absorptive changes in a single shot, with a time resolution approaching that of conventional pump–probe methodologies. Moreover, this new technique, which we call walk-off ring-down spectroscopy (WORDS), is easy to implement, can be regarded as self-calibrating, and is relatively inexpensive.

WORDS is a variant on cavity ring-down spectroscopy (CRDS), a highly sensitive direct absorption technique that has undergone a recent boom in spectroscopic applications. Just as in CRDS, WORDS measures the rate of decay of radiation inside a resonant cavity, and it does so in a way that permits absolute measurement of the concentration of absorbers in the resonant cavity. Much work has been done to characterize CRDS and to apply it to a number of different situations, such as to measure the kinetics of gas-phase chemical reactions [8], monitor radical intermediates in flames [9, 10] and plasmas [11], probe the structures of transient species in molecular beams [12], determine isotopic ratios [13], study interfaces [14], measure absolute absorption of solids [15], and, very recently, to measure absolute absorption [16–18] and kinetics [19] in liquids.

In a typical pulsed CRDS experiment, a beam is directed into an optical resonator comprised of two highly reflective mirrors. On each bounce, a small fraction of the radiation is transmitted through the mirror yielding a throughput whose intensity envelope follows an exponential decay [20]. The characteristic time constant of this decay (the time it takes the signal to fall to $1/e$ of its original value) may be related to the

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parameters of the resonator and sample by the following equation:

$$\tau = \frac{t_{\mathrm{rt}}}{2[(1-R)+\varepsilon[X]\ell]}, \tag{1}$$

where t_{rt} is the round-trip time within the cavity, R is the reflectivity of the mirrors (typically >0.999) and $\varepsilon[X]\ell$ is the familiar concentration-dependent Beer–Lambert law absorbance, where ℓ is the path length of the sample with concentration $[X]$ and logarithmic extinction coefficient ε. Traditionally, τ is referred to as the ring-down lifetime.

This process, depicted in figure 1, is the standard setup for a cavity ring-down experiment. At first blush, it seems that this type of experiment is unsuitable for studying ultrafast processes, principally because of the time contingent nature of the measurement. Specifically, the ring-down lifetime τ is typically on the order of a microsecond or longer. Logically, this method becomes problematic if we attempt to study processes faster than or comparable to the timescale over which the measurement is made. This problem is severe for the case in which only the intensity envelope is detected and the individual round trips are not resolved. However, when the pulses of the output train are discernible, they may be regarded as a series of single-pass measurements. As the absorptive properties of the sample change in time, so does the characteristic loss associated with each round trip. The time evolution of the absorbance can correspond to a variety of time-varying effects, including concentrations of the absorbing species and their molecular alignments. Any phenomenon that results in a time-dependent change in the optical losses $L(t)$ within the resonator can give rise to a measurable variation:

$$I(t) = I_0 \exp\left(-\frac{t_{\mathrm{r}}}{2[(1-R)+L(t)]}\right). \tag{2}$$

To distinguish between real fluctuations in optical losses and arbitrary noise effects, it is vital to account for the losses on each individual pass, information that cannot be easily extracted from the envelope function alone. The pulse train depicted in figure 1 must be resolved bounce by bounce. For processes occurring on timescales under a nanosecond, this task is not feasible with a conventional detection scheme utilizing a photomultiplier tube or a fast photodiode: the instrumental response time subsumes the resolution of the measurement. Prior to this article, our solution to the time response problem has been to use a streak camera or optical frequency mixing [21], both of which are able to monitor optical phenomena on a significantly faster timescale.

Recently, we have developed a much more economical means for performing these measurements. Moreover, this method even allows a higher time resolution than a streak camera. It shares the advantage of the streak camera in that it is self-calibrating, that is, each bounce can be compared to its predecessor.

Our method involves using an optical cavity oriented so that the beam does not retrace its own path along the longitudinal optical axis but rather 'walks' between the two mirrors, yielding a spatial progression of the output train that can be detected with a CCD camera, film, or any other imaging device having sufficient spatial resolution. The name of walk-off ring-down spectroscopy arises from this distinctive path. While this configuration does not constitute a stable resonator, its geometry does allow a facile conversion between space and time, thereby obviating the need for fast time-response electronics.

We present a comparison between this novel detection scheme and the ring-down signal yielded by on-axis alignment and detected with a streak camera. In both cases, the time resolution of the measurement is governed by the round-trip time within the cavity, which is determined by the mirror spacing. We find that the time resolution attainable by the WORDS method is superior to that of the streak camera by at least a factor of 5.

2. Experimental

Measurements using either a streak camera or WORDS were conducted with an actively mode-locked, argon-ion-pumped Ti:sapphire laser (SpectraPhysics) centered at 795 nm. Pulse duration was approximately 100 fs, and the average power incident to the cavity was 20 mW. Plane mirrors (CVI, $R=0.995$) were used to construct the optical cavity. The probe beam was sent into the cavity at a variable angle to the optical axis, according to the detection scheme. This experimental setup, with an arbitrary detection method, is depicted in figure 2.

The configuration of the optical cavity depends upon the means of detection. The axial scheme (figure 3(*a*))

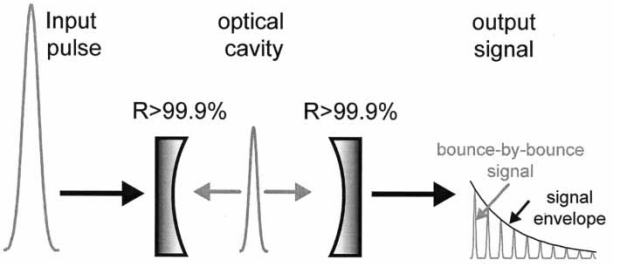

Figure 1. A simple model for CRDS.

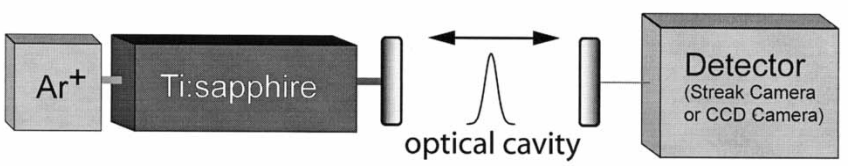

Figure 2. Output from a pulsed Ti:sapphire laser is directed into an optical cavity formed by a pair of plane mirrors. The time-dependent cavity output is then measured by the detection methods described in the text.

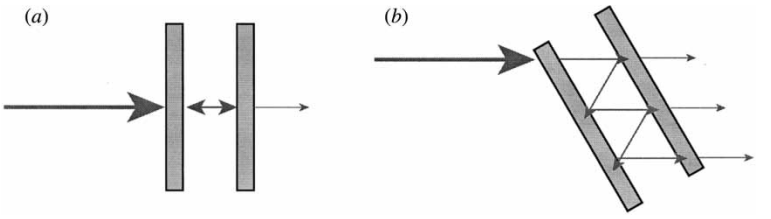

Figure 3. The two cavity configurations with respect to the incident beam. (*a*) The axial configuration may be employed in conjunction with a time-resolved detector. (*b*) The walk-off scheme circumvents limitations of temporal resolution by using geometry to turn a temporal measurement into a spatial measurement.

may be employed in concert with a fast-response detector, whereas the walk-off configuration (the simplest geometry of which is shown in figure 3(*b*)) is designed for time-insensitive detection methods.

For the axial case, the time-resolved output of the cavity was detected by means of a Universal Streak Camera (Hamamatsu Model C5680-01S) synchronously triggered to the repetition rate of the probe laser. One of the salient advantages of the streak camera is that it is able to monitor both temporal and spatial profiles of an optical signal. It is therefore ideal for measuring the time-resolved intensity decay of an on-axis ring-down profile. Output data takes the form of an intensity signal detected by a 512×512 CCD camera (Hamamatsu Model C4880), with one dimension corresponding to time and the other to one of the spatial dimensions transverse to the axis of the resonator. In the data here presented, the spatial portion of the intensity profile was partially filtered, restricting the integration area to the central region of the Gaussian profile. We achieved a time-dependent trace of the pulse train by integrating over the spatial component of the streak signal. A typical data trace was integrated for 100 ms, which corresponds to eight million shots per trace.

In the walk-off configuration, the basic principles of geometry are used to convert temporal variation into spatial variation. In its simplest configuration, a plane-parallel optical cavity is placed at an angle relative to the incident beam, as shown in figure 4, such that the beam traverses the surface of the mirror and the fractional transmission of each round trip emerges at a different point. The obliqueness of the angle between beam and optical axis is adjusted to obtain spatial separation of the consecutive pulses, and must be well known in order to determine accurately the round-trip time, which is given by

$$\Delta t = \frac{2L}{c \cos \phi}, \tag{3}$$

where L is the distance between the two mirrors, c is the speed of light in the medium enclosed by the cavity, and ϕ is the angular offset from the normal.

In the measurement reported in this article, the input pulse was directed into the cavity at an angle of approximately 20°, measured from the normal. The output was then directed into a lens and through a set of baffles before reaching the input aperture of a CCD camera (Hamamatsu Model C3640). The data were subsequently analysed by means of the same software that operates the streak camera. Essentially, the only difference between the instrumental setup of the two detection schemes is the orientation of the cavity and the replacement of the streak camera's temporal disperser with a lens.

Owing to the requirement of distinguishability of the output pulses, the spatial dimensions of the incident beam must be taken into consideration. For two adjacent pulses defined by the shape $f(x) = \exp(-x^2/a^2)$, we have defined the minimum threshold for separability as the displacement distance for which the net intensity achieves a second derivative greater than zero at some point between the pulses. Assuming parallel output trajectories, this displacement threshold is given by $s > 2^{1/2}a$. This theoretical lower limit diverges from the functional threshold as the optical losses within the WORDS cavity increase, but it serves as a useful guide for selecting the system geometry prior to

experimentation. Similarly, viable values of the angle of incidence relative to a plane-parallel cavity are defined by

$$\tan^{-1}\left(\frac{a}{2^{1/2}L}\right) < \phi < \frac{\pi}{2}. \quad (4)$$

For the data presented in this article, our beam was roughly 3 mm in diameter, and it was incident upon the cavity at an angle of 20° measured from the surface normal. The mirror spacing was approximately 500 μm, yielding a round-trip time on the order of 3.5 ps. The cavity itself was not an ideal plane resonator, but rather a wedge cavity, with the angular orientation of the back mirror offset fractionally from that of the front mirror. The benefits of this configuration are discussed in greater detail in the following section. As we show, the wedge helps to avoid problems that arise from the thickness of the probe beam.

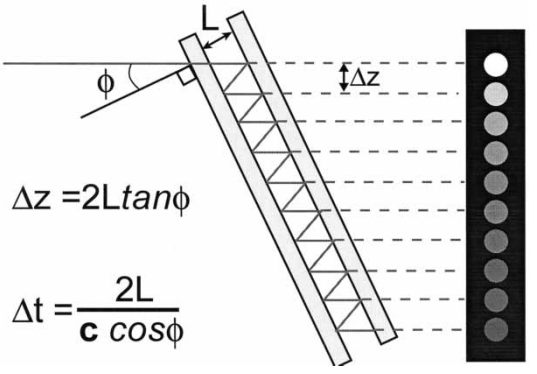

Figure 4. The timing of the spatially resolved throughput may be determined by basic geometrical arguments.

3. Results and discussion

Pulse-resolved ring-down measurements were performed for both of the detection schemes described in the previous section. The calibrated streak camera output was used as a standard of comparison. Typical data for this measurement, conducted in ethanol, are shown in figure 5 in one and two dimensions.

These data demonstrate excellent exponential behaviour – a linear fit to the logarithm of the peak amplitudes yields an R value of 0.999. The cavity length was slightly longer than 7 mm, corresponding to a round-trip time of about 30 ps in ethanol. The smaller secondary peaks, which are quite evident in the one-dimensional trace, arise from internal reflections within the back mirror. It is also noteworthy that the peaks appear to be of much longer duration than the 100 fs pulse time as measured by an autocorrelator. This apparent lengthening arises from a combination of frequency jitter and non-ideal coupling to the Ti:sapphire oscillator, which serves to trigger the field between the deflection plates within the streak camera's temporal disperser. Small fluctuations in laser frequency and line noise both serve to blur the temporal span of the pulse, lengthening its apparent duration to 15 ps or more. As the resolution of peaks becomes problematic for temporal separations shorter than the FWHM of the peaks themselves, this issue has imposed an unexpected limitation upon the optimal time resolution of the streak camera technique, effectively

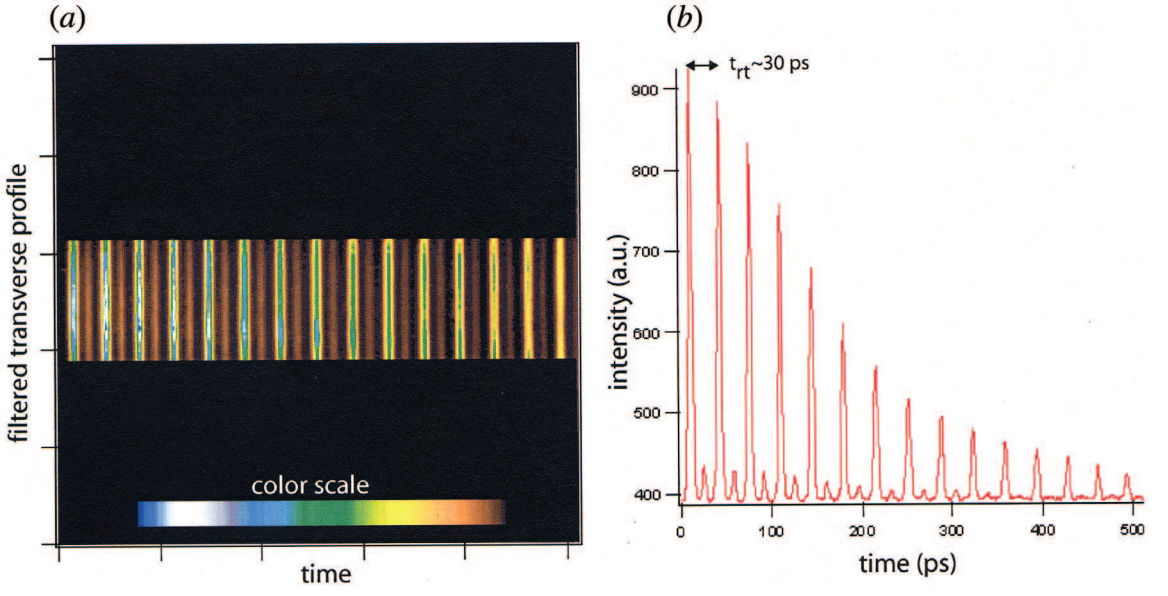

Figure 5. Ring-down profiles for the on-axis detection scheme: (*a*) two-dimensional with a false colour scheme and (*b*) spatially integrated.

decreasing it by at least a factor of 5 (a single pixel of the CCD output corresponds to roughly 1.5 ps, yielding a lower limit of 3 ps offset for separable peaks).

As a comparison, we have taken an analogous measurement with the WORDS configuration. The level of detail in the spatial profile is severely reduced, but such information is extraneous to the assessment of overall optical losses within the cavity. Free from the limitations imposed by the streak camera, we were able to use a significantly smaller cavity (~500 μm), yielding a round-trip time of < 4 ps in air. The trace is presented in figure 6.

As can be seen in the figure, the peaks are clearly resolvable with a time separation much shorter than anything accessible by the streak camera. The extent of their separation may be varied by changing the angular orientation of the cavity with respect to the incident radiation. Similarly, the time resolution of the measurement may be adjusted by changing the cavity spacing. In contrast to the streak camera, WORDS does not include a calibrated temporal measurement, which means that the cavity spacing must be known to a high degree of precision to obtain valid time constants. However, with careful experimental design, this method may be implemented with considerably lower expense than the streak camera configuration.

As a direct comparison, the best resolution we have been able to achieve with the streak camera is roughly 16 ps; smaller cavity spacing leads to a signal in which the individual pulses are inseparable. By contrast, we were able to achieve the 3.5 ps resolution demonstrated in figure 6 with virtually no efforts at optimization.

The attentive reader might notice that the number (~25) of round trips represented in figure 6 ought not to be resolvable under the experimental conditions outlined for a plane-parallel cavity in the previous section. Indeed, an ideal plane resonator that is 2.5 cm in diameter would not be able to achieve such clear spatial separation for a 3 mm beam. The superior resolution of our data is attributable to the fact that the cavity employed was, in actuality, a wedge rather than a plane-parallel cavity. Even a small tilt angle on one of the mirrors results in an output train with a progressive angular trajectory, enabling pulses that are overlapping in space (but not time) as they exit the cavity to be extricated from each other. This effect may be achieved by directing the optical throughput into a lens at a variable distance from the back mirror, as indicated in figure 7. The lens can then redirect the spatially separated signal onto the detector.

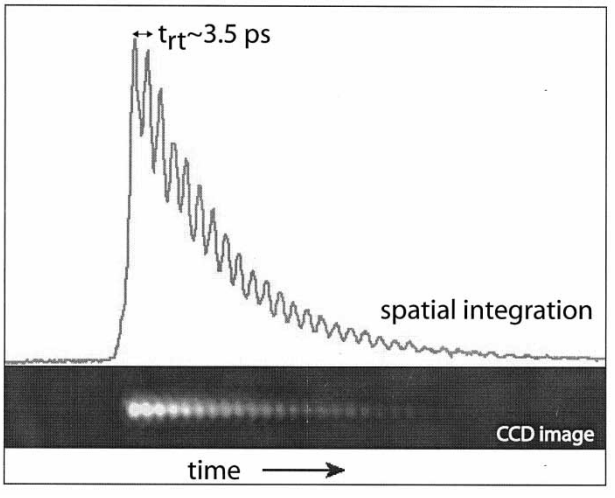

Figure 6. Ring-down trace obtained from the WORDS detection scheme. The full pulse, rather than a filtered portion, was used in the integration.

In the wedge cavity, each round trip may be expressed as a trajectory within a well-defined trapezoid. The geometric particulars for an arbitrary round trip (for which the beam path departs the back mirror at an angle $-\theta$ with respect to the normal plane of the front mirror) are presented in figure 8.

The wedge angle does not need to be large to achieve a noticeable effect. For a 3 mm beam normally incident to a 500 μm cavity, a 1° tilt on the back mirror can produce distinguishable peaks at a detector less than 20 cm away. Coupled with appropriate focusing optics, this configuration may be used to achieve far better resolution than would be possible with a perfect plane-parallel cavity. The time delay between bounces increases as the beam path grows progressively longer, but the most crucial interval for closely spaced measurements is early in the pulse train (assuming that for a pump–probe experiment, the pump is timed relative to the probe beam's initial pass). As a comparison, a 500 μm parallel cavity with a 20° angle of incidence yields 12 bounces in 40 ps as opposed to only 10 for the 1° wedge resonator, but the increased flexibility of the wedge with respect to beam shape more than makes up for this minor loss. While this characteristic is a distinct advantage from a practical standpoint, it also serves to underscore the vital importance of a well-understood cavity geometry if accurate temporal information is to be achieved.

Like any other technique, WORDS has its share of limitations. As with the streak camera configuration, the bounce-by-bounce analysis of the output train sacrifices a significant amount of the sensitivity that is touted as the touchstone of CRDS. Because each round trip is analogous to an independent measurement, the pathlength advantages of conventional cavity ring-down measurements are forfeited. This could pose a difficulty in the sense that to achieve faster time resolution requires shorter pathlengths, making it

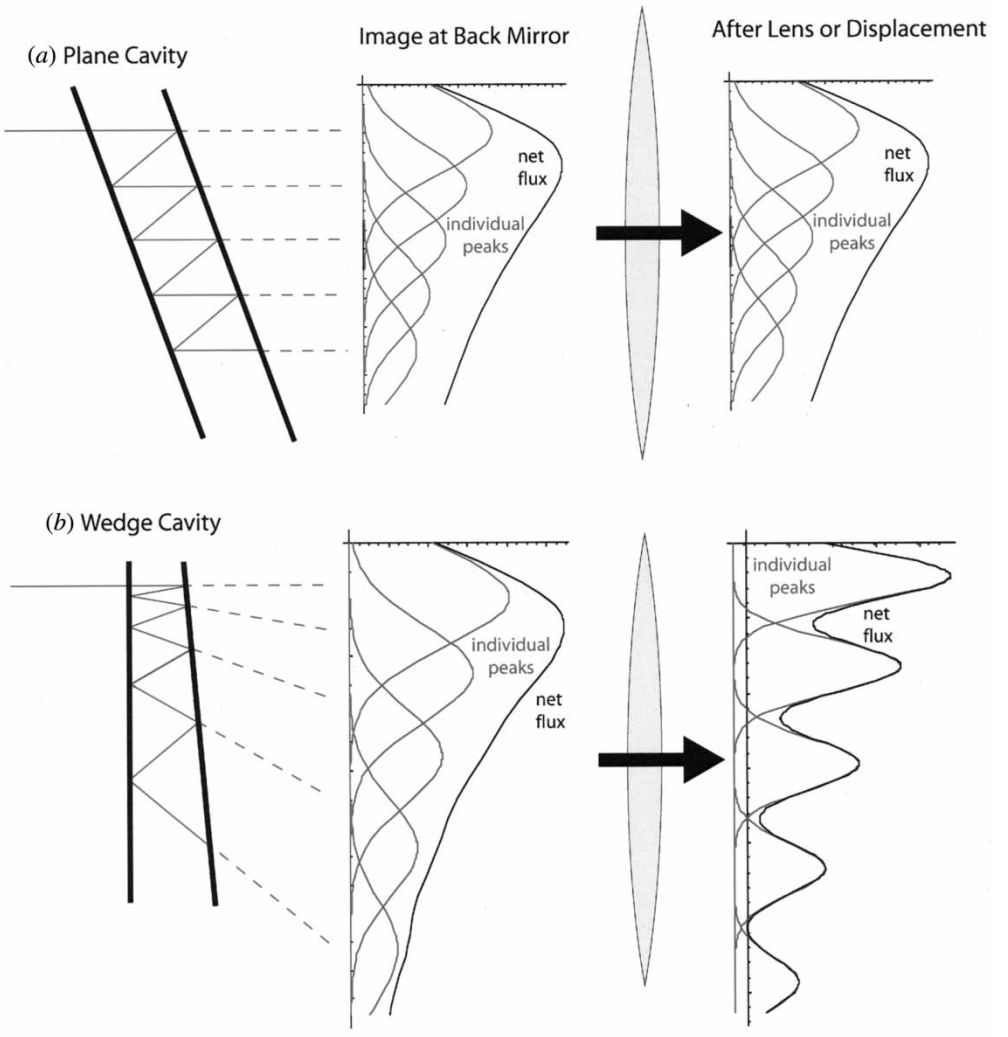

Figure 7. Spatial resolution effects of (*a*) a plane-parallel cavity as compared with (*b*) a wedge cavity. The nonparallel output train of the wedge cavity improves upon the limitations of spatial resolution arising from pulse overlap caused by the finite thickness of the probe beam.

progressively difficult to observe small changes in optical absorption. Nevertheless, bounce-by-bounce CRDS holds an advantage over the detection limitations experienced by single-pass experimental configurations because of the self-calibrating nature of the measurement. In particular, because each output pulse may be normalized to its predecessor and analyzed in the context of the ring-down as a whole, fluctuations in laser power are less problematic than in the single-pass regime.

Another feature of WORDS is that typical measurements will employ somewhere between 5 and 50 bounces. Consequently, the reflectivity constraints of conventional CRDS, which typically involves thousands of bounces or more, do not apply, and we can use mirrors with larger transmission values. Indeed, signal-to-noise considerations suggest that these poorer quality mirrors are to be preferred, reducing costs and extending the wavelengths coverable by WORDS. The assumption of self-calibration is contingent upon the uniformity of the mirrors' reflective coating, namely that the fractional losses due to mirror transmission do not change with the spatial progression. Given the consistency and quality of the mirrors available, we do not anticipate this to be a problem. However, it is an issue that should not be overlooked when selecting mirrors for use in WORDS.

A second important consideration is the evolution of the beam's characteristics as it propagates through the sample. Dispersion – the temporal lengthening of the beam – is potentially problematic should the probe begin to overlap itself in time, i.e. if the duration of the beam becomes longer than the round-trip time for a given pass. However, this situation is another for which the

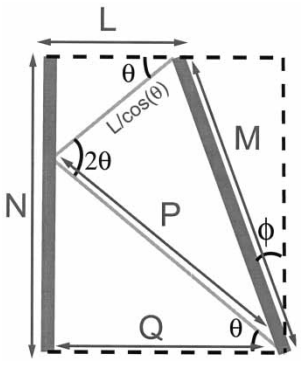

Figure 8. Trapezoidal configuration of an arbitrary round trip within a wedge cavity whose back mirror is offset by an angle ϕ. For a beam incident perpendicular to the front mirror, the trajectory angle, θ, increase as $\theta = \phi(n + 1)$ for the nth bounce. The values of the lettered quantities in the figure are as follows:

$$M = \frac{2L\sin\theta}{\cos(\phi+\theta)}, \quad N = \frac{2L\sin\theta\cos\phi}{\cos(\phi+\theta)\cos\theta},$$
$$P = \frac{L\cos(\phi-\theta)}{\cos(\phi+\theta)\cos\theta}, \quad Q = \frac{L\cos(\phi-\theta)}{\cos(\phi+\theta)}.$$

wedge cavity poses a potential advantage: although the probe disperses as it propagates, the round-trip time within the wedge increases as well.

Another optical effect that could potentially impact the viability of bounce-by-bounce CRDS, particularly in liquid samples, is thermal lensing. Thermal lensing is a well-studied phenomenon that arises from the propagation of a high peak power pulse through a solution containing a strong absorber. The absorbed light is nonradiatively transferred to the solvent as heat, creating a gradient in temperature T transverse to the beam path and a corresponding gradient in refractive index n:

$$\Delta n = \Delta T \frac{\mathrm{d}n}{\mathrm{d}T}, \tag{5}$$

where $\mathrm{d}n/\mathrm{d}T$ is a fixed property of the solvent. In consequence, the heated sample functions as a convex lens (for typically negative $\mathrm{d}n/\mathrm{d}T$ values) and the beam spreads out as it resamples the heated region. In the on-axis configuration, this self-lensing effect is compounded by the multiple round trips within the cavity. When the output train is spatially filtered or expands beyond the streak camera's very limited window of acceptance, this phenomenon can result in skewed peak amplitudes and consequently a misrepresentation of the true ring-down lifetime. Self-lensing becomes more important at higher power, and while it may be avoided by careful control of the experimental conditions, such precautions may serve to reduce the measurement's dynamic range.

The walk-off scheme is less drastically affected by such lensing phenomena. Because the beam does not retrace its own path, it largely eludes the index of refraction gradient produced by previous passes. This advantage is particularly relevant at longer effective path lengths because the thermal lens effect becomes increasingly apparent the longer the beam propagates within the lensing medium. Naturally, self-lensing effects cannot be completely eliminated; in particular, the (typically minute) distortion produced by the front of the pulse will affect the back of the pulse regardless of the beam path. However, the WORDS technique does serve to minimize those effects that are exacerbated by the geometry of the linear cavity.

To utilize the WORDS methodology for ultrafast measurements, the probe system must be coupled with a pump event. As with conventional pump–probe spectroscopy, this requires directing the pump and the probe into the sample at a well-known delay. However, whereas conventional techniques only provide one delay measurement per pump event, WORDS can yield up to 50 or more. The chief consideration here is to ensure that the probe beam is monitoring the consequences of a consistent pump event – the pump field must be uniform throughout the region sampled by the probe. This can be accomplished either by a broadened, transverse beam or by a collinear beam incident to a dichroic cavity, which is reflective for the probe light but transparent at the pump wavelength. As with the transverse configuration, the collinear beam must have a sufficient spatial expanse to provide a uniform excitation field throughout the region explored by the probe.

Currently the greatest drawback of the WORDS method as compared with existing pump–probe techniques is that of temporal resolution. The use of delay stages between pump and probe permits acute control of their relative timing. However, there is no reason that such methods could not be incorporated into the bounce-by-bounce CRDS methodology. By controlling the delay between the incident pump and probe pulses, it becomes possible to monitor simultaneously two distinct timescales. The time resolution may be improved twofold from the apparatus here presented by detecting the pulse train emitted from both mirrors of the cavity, but the technique is fundamentally constrained to the measurement of events that occur on timescales longer than the pulse duration.

4. Conclusions

Walk-off ring-down spectroscopy (WORDS) is a novel technique, based on converting temporal measurements into more easily measured spatial measurements, for achieving time-resolved measurements without the

use of a fast-response detector. It has been demonstrated to perform at a better time resolution than the streak camera as a detection scheme for pulse-resolved CRDS, and may be implemented with considerably less expense. In addition to low cost, this method provides the additional advantage of minimizing the problematic lensing effects that impose severe limitations upon the on-axis scheme in condensed media. Implementation of the existing method into the pump–probe regime for ultrafast measurements requires a precise knowledge of the cavity geometry and a highly uniform pump field throughout the progression region. The preliminary success of the WORDS technique shows it to have great promise as a novel methodology for measuring ultrafast photophysical phenomena.

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