Evanescent field absorption in a passive optical fiber resonator using continuous-wave cavity ring-down spectroscopy

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Abstract

We combine the sensitivity advantages of cavity ring-down spectroscopy (CRDS) with the versatility of optical fiber sensing technology in a spatially extended passive fiber ring resonator constructed of common telecommunications components. The resonator is characterized with both pulsed and continuous-wave diode laser excitation, and it is shown to be a practical device for direct measurement of loss in a fiber-optic system as well for CRDS sensing in liquids. We demonstrate a minimum detectable loss of 0.017% per √Hz and show near-infrared absorption of 1-octyne with a minimum detectable concentration of 0.049% per √Hz in non-interacting solvent at 1532.5 nm.

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1. Introduction

The high sensitivity of cavity ring-down spectroscopy (CRDS) has propelled its development in recent years [1], though little progress has been made in extending its utility beyond localized detection. Conversely, the versatility of optical fiber chemical sensing has broadened its application into a variety of new fields [2], but its use is constrained by the limited sensitivity of common single pass measurement techniques. These two technologies have recently been combined in investigations of optical fiber CRDS resonators for the measurement of several parameters including bending loss [3,4], direct path absorption [5], and evanescent field attenuation [3,4]. We have developed a new spatially extended fiber ring resonator composed of common telecommunications components and demonstrate its utility as a practical device for CRDS and evanescent field absorption spectroscopy.

A typical CRDS device, formed by two highly reflecting mirrors, measures changes in the decay time of an optical resonator after excitation with pulsed laser radiation. The corresponding decay rate is proportional to the resonator’s losses, allowing quantitative detection of absorbing species contained between the mirrors. The determination of rate, which is not directly influenced by cavity excitation intensity, reduces susceptibility to sources of noise that are common in absorption spectroscopy, such as source amplitude fluctuations and interference from external absorbers [6]. Additional signal-to-noise improvement can be gained with single mode continuous wave (CW) excitation [7]. High characteristic sensitivity, coupled with the inherent selectivity of optical absorption spectroscopy, account for the wide application of CRDS to a variety of sensing problems, ranging from resolution of forbidden overtone transitions in small molecules [8] to quantification of trace concentrations of atmospheric particles [9].

Optical fibers have also been employed in an assortment of spectroscopic applications and are suited for use in CRDS. Typical single mode fiber, common in communications systems, has low attenuation and supports only the lowest order transverse mode, making it appropriate for use in CW-CRDS resonators, where minimal loss is required and single mode excitation improves stability. This type of fiber is also compatible
with a variety of inexpensive, rugged components, which are designed for low loss communications systems and are adaptable to chemical sensing. Implementing such components in a CRDS system reduces tedious cavity alignment and improves mechanical stability. Furthermore, the long distance transmission capacity of single mode fiber combined with its flexibility in diverse sensing configurations can be exploited to expand the utility of CRDS to a variety of novel conditions. Among these potential new applications for CRDS are sensing in liquids; distributed sensing, in which sensors are deployed over a wide area; and standoff detection, in which control and acquisition components are separated from a remote sensing location.

Despite the advantages of single mode fiber, most fiber optic chemical sensors are made of multi-mode fiber because it provides easier access to the evanescent fields used in sensing. However, single mode fiber can be modified to enhance evanescent fields in its cladding while maintaining the modal selectivity necessary for CW-CRDS. A biconic taper formed in a section of fiber serves as a low loss sensing element in which a cladding mode is excited and then reconverted into the lowest order propagating mode [10]. Formed by heating a section of the bare fiber to its softening point and drawing along the fiber axis for a predetermined distance, a taper can be fabricated with little excess loss by avoiding abrupt changes in diameter or discontinuities in the fiber surface [11]. Careful design of the taper parameters, including overall length and minimum waist, allows specification of either evanescent field enhancement for higher measurement sensitivity, or minimal field exposure for an extended concentration sampling range. In addition, a carefully designed bend in the tapered region increases the penetration depth of the evanescent field, further improving sensitivity [12].

A tapered sensing region is a simple modification that adapts single mode fiber for chemical sensing and makes it useful in a CRDS resonator. We have designed and tested a device based on a combination of this single mode fiber sensing technology and CW-CRDS to gain the general versatility of fiber optics and the improved sensitivity of CW-CRDS. The simple, low cost device, constructed from off-the-shelf telecommunications components, uses a long physical resonator, several kilometers in length, both to allow distributed sensing and standoff detection and to increase ring-down times for greater ease of signal detection. We determined the resonator’s stability and demonstrated its feasibility for evanescent field absorption spectroscopy by measuring the spectral profile of a near-infrared absorption line. By implementing CW-CRDS in an extended fiber optic resonator, we establish the practicality of gaining the benefits of both technologies, including high sensitivity and broad versatility, while opening the potential for new sensing schemes not accessible with a localized resonator.

2. Experimental

The fiber ring-down apparatus, Fig. 1, was designed to include a minimum of custom components in an effort to minimize cost and increase overall versatility. The resonator is constructed from a 2.2 km length of standard single mode fiber (SMF-28e, Corning, Inc.) that is fusion spliced (FSU 975, Ericsson, Inc.) to two input/output couplers (Lightel Technologies, Inc.). The couplers, used in place of the mirrors in a traditional resonator, each have a 99%/1% split ratio to provide directional input and output coupling of the resonant radiation and to give a reasonably long ring-down time. Although we use two couplers for convenience, system loss could be further minimized using a single coupler with a fast switch before the detector to avoid saturation while the cavity is excited. The resonator is modified for evanescent field sensing by fusion splicing a custom made fiber taper (Lightel Technologies, Inc.) between the two couplers. The taper, having a 10 μm waist diameter and 28.0 mm overall length, is bent to enhance the localized evanescent field and improve sensitivity.

The resonator is excited by a narrow-band diode laser, which is amplitude switched by rapidly (<1 μs) reducing the drive current below operating threshold, allowing direct detection of the cavity ring-down signal. The laser is optically isolated from the rest of the system by a dual stage 60dB Faraday isolator (Lightel Technologies, Inc.) placed immediately before the input coupler to prevent destabilizing feedback from back-reflections of the fiber connectors. At the other end of the resonator, the cavity output is detected with an InGaAs detector, amplified by a 700 kHz bandwidth amplifier, and sampled on a digital oscilloscope. For resonator stability measurements, the detected signal is

![Fig. 1. Schematic diagram of the passive optical fiber CW-CRDS system.](image-url)
The optical decay time of our fiber ring resonator can be derived starting with the general expression for the decay time, \( \tau \), of a linear CRDS cavity due to its intrinsic losses [1]

\[
\tau = \frac{t_R}{2(1 - R)},
\]

where \( t_R \) is the round trip time of the cavity and \( R \) is the power reflectivity of the mirrors. When the cavity is filled with an absorbing species, an additional term is added to the expression for ring-down time [1]

\[
\tau = \frac{t_R}{2[(1 - R) + \alpha L]},
\]

in which \( L \) is the cavity length and \( \alpha \) is the absorption coefficient of the species contained within the cavity. To adapt this to the case of a unidirectional fiber resonator, the expression is first generalized to describe the intrinsic losses of the system and additional loss due to external absorption, and then separated into terms representing the individual components

\[
\tau = \tau_{\text{coupler}} + \tau_{\text{fiber}} + \tau_{\text{splice}} + \tau_{\text{taper}} + \tau_{\text{abs}},
\]

in which \( \tau_{\text{coupler}} \) is the combined insertion and coupling loss of the two couplers; \( \tau_{\text{fiber}} \) is the transmission loss of the fiber; \( \tau_{\text{splice}} \) is the loss from the four fusion splices used to join the components; and \( \tau_{\text{taper}} \) is the insertion loss of the tapered sensing region. An additional term, \( \tau_{\text{abs}} \), is used to describe the loss due to an external absorber in the evanescent field surrounding the taper.

In the limit of weak external absorption, the loss due to absorption by an external species, \( \tau_{\text{abs}} \), is directly proportional to both the molecular absorption strength of the analyte and the power of the field exposed by the taper [13]. These two factors can be combined in the calculation of an attenuation coefficient that describes the loss in the propagating core mode. This coefficient, generalized for the \( j \)th propagating mode, \( \gamma_j \), is described by [14]

\[
\gamma_j = 2k \left( \frac{\varepsilon_0}{\mu_0} \right)^{1/2} \frac{\int_{dA} n_j^n n_j^l |e_j|^2 dA}{\Re \left\{ \int_{dA} e_j \cdot h_j \cdot \tilde{\gamma} dA \right\}},
\]

in which \( k \) is the magnitude of the wavevector of the propagating field, or \( 2\pi/\lambda \), where \( \lambda \) is the free-space wavelength; \( n_j^n \) and \( n_j^l \) are the real and imaginary parts of the index of refraction of the fiber; \( e_j \) and \( h_j \) are the electric and magnetic components of the \( j \)th mode; and \( A \) represents the cross sectional area of the fiber and surrounding region. Because higher order modes are lost at the end of the taper, and their excitation is therefore included in the intrinsic loss of the taper, determination of the behavior of the lowest order mode gives an ac-

3. Results and discussion

3.1. Principle of operation

Cavity ring-down measurement in a fiber ring resonator with a tapered sensing region requires modification of the general expression for ring-down time in a CW-CRDS resonator. An expression describing the optical decay time of our fiber ring resonator can be

Further sampled by a 12 bit analog-to-digital conversion card and is fit to an exponential decay using a custom fitting routine that includes statistical characterization of individual ring-down transients. For all other measurements, the oscilloscope signal is fit using a separate non-linear least squares fitting routine.

Initial experiments with this system focused on the characterization of the fiber resonator with an external cavity diode laser (ECDL) centered at 1550 nm (Tunics Plus, Nettest, Inc.) using pulses shorter than the round trip time of the fiber ring. After characterization of the resonator with pulsed excitation, all other work was carried out with CW excitation, in which the laser emission time is significantly greater than the decay time of the resonator. Analysis of resonator decay under both CW and pulsed operation was undertaken with the same ECDL to ensure accurate performance comparison of the two approaches in ring-down time and signal-to-noise response. The stability of the system, used to indicate minimum sensing levels, was also established in the CW configuration by measuring repeated transients with a distributed feedback (DFB) laser (Model #NLK1556STG, 1520 nm; NEL America, Inc.) and comparing ensembles of differing numbers of ring-down times.

The fiber system was then tested with the broad wavelength tuning range of the ECDL for evanescent sensing of the spectral profile of a molecular absorption band. The dimensions of the tapered sensing region, 28 mm long with a 10 \( \mu \)m waist, were chosen both because of the relative insensitivity to bend loss due to its long, and thus gradual, taper length and because of its complete conversion of the fundamental core mode to an evanescent cladding mode based on the minimum waist diameter. The bent taper was immersed in 1-octyne, and the ECDL wavelength scanned from 1520 to 1550 nm. To ensure accurate positioning of the measured absorption lines, the results were qualitatively compared with a low resolution scan of 1-octyne acquired on a FT-IR spectrometer (Nicolet 730) with a 1mm path length cell. A plot of absorption strength as a function of concentration was also acquired on the low resolution spectrometer, and the results were compared with the fiber resonator signal for determination of minimum detection limits.
curate picture of the attenuation due to absorption. For the size tapers that we use, the core is too narrow to guide the propagating mode, and we can treat the fiber cladding as the new core with a constant index of refraction and the medium surrounding the fiber as the new cladding. The text by Snyder and Love [14] gives expressions for the loss of the modes of this waveguide in terms of the absorption coefficients of the core and cladding and the propagation constant for each mode. We calculate the latter for the lowest order mode and a range of separate core diameters by solving a transcendental equation. Neglecting the intrinsic loss of the fiber, the attenuation coefficient of the fundamental mode decreases rapidly with increasing fiber radius due to reduced fractional energy penetration into the sample. Fig. 2 gives a plot of the ratio of the effective absorption coefficient of the lowest order mode divided by the absorption coefficient of the sample indicating the higher sensitivity to absorption with a narrow taper waist. For the taper used in our device, which is assumed to have a parabolic profile with a 28.0 mm length and 10 μm minimum waist, we integrate the power attenuation coefficient, \( c \), along the taper length to find an effective absorption length of 100 μm. This represents a 200-fold improvement per pass over other evanescent wave CRDS devices, assuming a sampling depth of 0.5 μm, typical for an evanescent wave device operating at this wavelength [15–17]. This can be further improved by decreasing the waist diameter, though tapers of smaller waist are quite fragile and thus difficult to work with. The fractional field exposure can also be increased by bending the taper, but we have not quantitatively modeled this effect. The magnitude of the attenuation coefficient, which varies linearly with absorption coefficient, indicates the limitations of optical fiber sensing but also shows the importance of using a sensitive detection scheme such as CRDS.

3.2. Experimental results

We first demonstrated the performance of our system with pulsed excitation both as a comparison to other reported fiber resonators and because of the inherent simplicity of pulsed CRDS. Pulsed laser excitation, produced by switching the laser current with pulses shorter than the round-trip time of the fiber ring, gave a voltage signal-to-noise ratio of 40:1 (32 dB) with a 10 mW laser. The corresponding resonator output, Fig. 3, was analyzed by assuming a Gaussian shape for each resonator pulse and fitting their decaying amplitudes to a single exponential decay with ring-down time of 48.98 μs and a 2.5 μs rms standard deviation in the fitted points. Such characterization allows a direct way to measure total optical loss in the system; the measured ring-down time corresponds to a total loss of 21.7% per round trip. Although this high intrinsic loss of the resonator significantly reduces the ring-down time, its physical length balances the effect to permit slower detection and acquisition components. The extended resonator, which contributes a round trip loss of only 9% from the bulk attenuation of single mode fiber, facilitates a simpler signal processing scheme and allows the use of a lower bandwidth detector with reduced noise equivalent power. The size of the resonator also extends the applicability of this system to standoff detection or distributed sensing with the introduction of several sensing elements along the resonator length.

The extended resonator configuration also simplifies the implementation of amplitude-switched CW excitation, a way of improving signal-to-noise output and enhancing sensitivity. Amplitude switching of CW diode lasers, which have relatively slow recovery rates, is not compatible with previously reported optical fiber reso-
nators that are on the order of 1 m in length. Although DFB lasers can be modulated at rates on the order of 1 GHz, switching between the laser threshold current and maximum power is not possible at such high rates using conventional laser drivers. Typical methods of complete laser amplitude modulation that have rise times on the order of 1 μs, such as acousto-optic or drive current modulation, become accessible with the long physical resonator. We demonstrate such CW excitation with our system, Fig. 4, by electronically modulating the ECDL source. The resultant ring-down signal has a voltage signal-to-noise ratio of 120:1 (42 dB) and is fit by an exponential decay with ring-down time of 52.28 μs and a 0.375 μs standard deviation in the fitted points, an improvement over the pulsed architecture in each measurement.

Despite the expected signal enhancement and improved resonator stability with CW excitation, the resonator output shows step features. These steps are not observed in mirror based CW-CRDS because they are easily filtered out from the ring down decay. In this system, they cannot be avoided due to the high loss of the couplers and fusion splices encountered in each round trip of the fiber resonator. The resonator output can be described by the function

\[ F(t) = F(t_0) R \text{Int}(\frac{t - t_0}{l}) \]

where \( R \) is the resonator loss, \( t_0 \) is the time at which the laser source is switched off, and \( l \) is the round trip time of the resonator. Although this function conveniently gives a direct measure of the resonator loss, we convert this to a ring-down time for a more meaningful comparison with other data. Such comparison shows a difference in decay times of up to 10% between the two models, indicating significant inaccuracy in the measurement of absolute system loss when using the measured ring-down time with an exponential model. However, the variation in decay times within each model show the precision in the fits to be much better. Using measurements taken at 1550 nm, the step model shows an average standard deviation in the fitted points of 0.40% of \( \tau \), while the single exponential decay model shows a standard deviation of the fitted points of 0.73% of \( \tau \). The standard deviation in the fitted points are somewhat conservative, as the data points are not completely independent due to the slightly greater sampling rate relative to the detector time constant. Although this factor is not large with our data acquisition components, statistical comparison of several ring-down transients gives a more realistic indication of the system sensitivity. The step model shows an ensemble standard deviation over 16 decays of 0.9% of \( \tau \), while the exponential model has an ensemble standard deviation of 1% of \( \tau \), indicating the practical sensitivity of the system for comparative measurement.

The similar precision of the ensemble measurements suggests the suitability of a single exponential decay to approximate the resonator output for measurements using a taper with a calibrated initial loss. Such a fitting routine has the additional benefit of being easily linearized, reducing computational fit time and allowing long-term averaging to reduce noise and improve sensitivity. The long-term stability of the system, indicating the feasibility of extensive averaging, was measured using an electronically modulated DFB laser centered at 1520 nm. With this system, an exponential fit to a single decay has a standard deviation in the fitted points of 0.236 μs in a 47.18 μs decay, while collections of 25, 100, and 250 decays show ensemble standard deviations of 0.771, 0.616, and 0.601 μs, respectively. The lower standard deviation for the single decay indicates that ring-down measurement in the fiber system is not significantly affected by the simplicity of the fit, while the long-term stability suggests the compatibility the system with extensive averaging to further enhance sensitivity.

The sensitivity of the system to small changes in ring-down time is complemented by the effectiveness of the tapered sensing region for evanescent field absorption sensing. By using the extended scanning range of the ECDL, the system was able to resolve the overtone absorption line of 1-octyne centered at 1532.5 nm, Fig. 5. Comparison of the ring-down scan with low resolution data, acquired on a FT-IR spectrometer, shows qualitative agreement in both absorption strength and wavelength. The small peak centered at 1541.5 nm is likely due to impurities in the sample or excitation of ‘hot band’ transitions. This resolution of spectroscopic features confirms sensitivity to absorption, instead of refractive index changes, which can complicate evanescent field detection.

Fig. 4. Continuous-wave ring-down curve. Fit of raw data shows \( \tau = 52.28 \pm 0.375 \) μs. Inset shows comparison of step-fit model and single exponential decay model over a shorter time scale.
The difference in experimental ring-down times over the 1-octyne scan at both on- and off-resonance wavelengths indicates the sensitivity of the system for absorbance measurement. An on-resonance ring-down time of 25.14 µs at 1532.5 nm shows an additional loss of 15.5% per round trip compared to the off-resonance ring-down time of 39.73 µs at 1550 nm. The standard error in the ring-down time estimated from 16 decays, defined as the standard deviation divided by the square root of the number of samples, is 0.1878 µs at 1532.5 nm and 0.0997 µs at 1550 nm. This indicates a minimum detectable loss, equal to twice the standard error, of 0.133%, corresponding to a minimum detectable concentration of 1.05% 1-octyne in a non-interacting solvent such as decane. Assuming 1000 decays can be measured per second, this sensitivity can be further reduced by averaging to a minimum detectable loss of 0.017%, or 0.049% per √Hz of 1-octyne.

Comparison with the minimum measured ring-down time shows the accuracy of the modeled loss. Using the estimated evanescent sampling length, calculated by integrating the attenuation coefficient over the length of the taper, we predict a loss due to absorption of 13%, based on a measured molar absorptivity of 3700 L mol⁻¹ cm⁻¹ at 1532.5 nm. This is only slightly lower than the measured loss of 15.5%, indicating the validity of the modeling assumptions. The lower calculated loss can be attributed to such assumptions, including the uniformity of the taper shape, the minimum taper waist, and the absence of defects that would disturb the propagating mode. Additional absorption loss due to the greater field exposure in a bent taper, which is not included in the model, also limits the estimation.

The measured absorption detection limit, although poor for typical CRDS measurements, is comparable to evanescent wave spectroscopy work done with other molecules in the mid-infrared region [18,19]. A literature comparison does not exist for 1-octyne, but other examples in the mid-infrared region show detection limits on the order of a few percent. The magnitude of this limit arises from both the increased absorption strengths in the mid-infrared, which are several orders of magnitude stronger than in the near-infrared, and the increased penetration of the evanescent field at longer wavelengths. Given this, our fiber based CRDS device shows an improvement in detection limit over other ATR techniques, although a more meaningful comparison could be made with a surface-modified measurement, a more common use of ATR elements [20,21]. Such techniques, involving customization of the taper surface for molecular recognition and concentration, are the best way to improve the sensitivity of this CRDS device, as they take advantage of its capacity for near-field sampling.

4. Conclusion

We have demonstrated an extended optical fiber resonator made from off-the-shelf components and show that, with minor modifications, the resonator can be adapted for evanescent absorption sensing. Although further improvements, such as customized lower-ratio couplers, can improve the optical decay time of the resonator, we show that such changes are not necessary for evanescent absorption sensing. This method of evanescent field access, while not especially suited for trace measurement of bulk liquids, shows improvement over other direct measurement evanescent wave spectroscopy techniques. In addition, the length of the resonator has the capacity to extend CRDS measurement from localized devices to distributed sensors that take advantage of the adaptability of fiber optic technology. This CRDS system also holds significant potential for near-field sensing in films or coatings on the fiber surface, which could improve sensitivity and further extend its use. This simple, inexpensive device combines the versatility of optical fiber sensing with the benefits of CRDS detection, including immunity from external absorbers, lower sensitivity to source amplitude fluctuations, and higher spectroscopic resolution.

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References


