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Derivation of New Equations for Phase-Shift Cavity Ring-Down Spectroscopy

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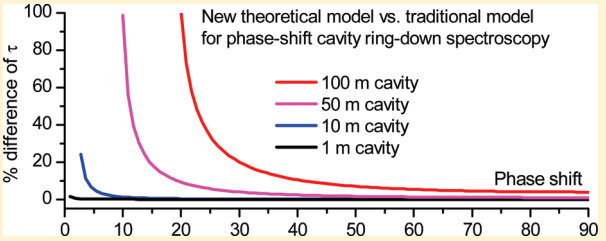
ABSTRACT: Current phase-shift cavity ring-down spectroscopy (PS-CRDS) experiments make use of equations originally developed for fluorescence studies. As these equations fail to take the length of the optical cavity and the superposition of reflecting beams into account, they lose validity as the length of the cavity increases. A new set of equations, based solely on the principles of PS-CRDS, is developed for determining the ring-down time from either the phase shift or the intensity of the waveform exiting the cavity. It is shown that the PS-CRDS equations reduce to those developed for fluorescence study for short cavities. The new equations provide a more accurate method in determining the characteristic ring-down time and phase shift for long cavities, especially fiber optic cavities, which is promising in on-site chemical sensing.



1. INTRODUCTION

Cavity ring-down spectroscopy (CRDS) is a powerful analytical tool which can be effectively used to detect weak transitions in concentrated samples or strong transitions in very dilute samples.[1−4] Although CRDS cannot compete in terms of sensitivity with laser-induced fluorescence (LIF) or resonance-enhanced multiphoton ionization (REMPI), it is more versatile and may be applied in situations where LIF or REMPI would be impractical or impossible.[1]

In pulsed CRDS (P-CRDS), a pulse of light several nanoseconds in length is coupled into an optical cavity defined by two highly reflective mirrors. As the light traverses the cavity, it is attenuated through repeated interaction with the cavity mirrors and chemical absorption. A detector on the opposite side of the cavity, usually a photomultiplier tube, detects the light transmitted through the rear-cavity mirror, producing a series of delayed pulses, the maxima of which may be used to fit an exponential decay function. From this curve fit, the characteristic ring-down time of the cavity for a given sample at a particular wavelength can be determined. Therefore, it is possible to make indirect measurements of either the concentration or the absorbance coefficient of the sample at a given wavelength.

Rather than coupling discrete pulses into the optical cavity, continuous-wave CRDS (CW-CRDS) uses a continuous-wave (CW) laser to build up intensity within the cavity.[3,5,6] In practice, this means that either the laser wavelength must be mode-matched to the length of the cavity or that the cavity be designed to have a near continuum of modes.[1] The latter may be achieved by constructing the optical cavity so that the ratio of the mirror radius to mirror separation is irrational.[1] Once the light within the cavity has built up sufficient intensity, the laser is decoupled from the cavity, and the exponential decay of the light exiting the cavity is measured by the detector. Because the light within a CW-CRDS setup is built up over time and few cavity modes are excited, the technique tends to produce higher-quality spectra than those produced by P-CRDS.[1]

Phase-shift CRDS (PS-CRDS) is an indirect method that uses the phase shift between the signals entering and exiting the optical cavity to determine the ring-down time of the sample. In 1980, Herbelin et al. first developed a phase shift method with a modulated laser beam for measuring photon lifetime in an optical resonator.[7] In 1996, Engeln et al. used the technique of PS-CRDS to measure the transition frequencies of a very weak transition of $^{18}O_2$.[8] In 2002, Hamers et al. combined PS-CRDS and Fourier transform spectroscopy, resulting in a sensitivity increase of approximately 3 orders of magnitude when compared to standard Fourier transform spectrometers.[9] Tong et al. developed a phase shift method for fiber loop ring-down spectroscopy and applied it as an absorption detector for a flow system with a short absorption path length in 2004.[10] Later, van Helden et al.[11] and Kasyutich et al.[12,13] improved the quantitative accuracy of PS-CRDS by eliminating the interference from amplified spontaneous emission (ASE) of the laser.

The idea of using the phase shift between input and output signals to measure the time constant of a decay system is not native to CRDS. Rather, the method was originally developed in 1933 by F. Duschinsky for the purpose of measuring fluorescence decay times.[14] The equations developed in his paper described a system in which a flat fluorescing sample was excited by a modulated light source. When the intensity of the light source was modulated periodically with respect to time, the fluorescence of the sample was found to vary with the same frequency but with a phase shift related to the decay time of the system.

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With the development of PS-CRDS, F. Duschinsky's equations were readily adopted by Herbelin et al., Engeln et al., and others due to similarities between the two systems.[7−10] Recently, Bescherer et al. derived the same equations for multiexponential optical decay processes using Laplace transform of the input beam.[15] However, because Duschinsky's equations assume that the fluorescent system has no internal dimension, they fail to take into account the time that light requires to traverse the cavity in CRDS. As a direct result, the phase differences between reflected waves inside of the cavity are not continuous as assumed in the fluorescence equations but are functions of cavity length, modulation frequency, and the speed of transmission. Although these changes are found to be negligible for short cavities, they can lead to large inaccuracies for long cavities or cavities with high-density media in which the speed of light transmission is reduced (such as fiber-optic-based systems).

2. THEORY

2.1. Phase Shift in Fluorescence. The fluorescent system has been previously modeled[8,9] through the use of equations developed in 1933 by F. Duschinsky.[14] The intensity of a sinusoidally modulated light beam entering the system is given by

$$P_{in}(t) = I_0[1 + \alpha \sin(\omega t)] \quad (1)$$

where t is time, $\alpha \leq 1$ is the relative depth of modulation, ω is the angular frequency of modulation, and I_0 is the center amplitude (intensity offset above 0) of the excitation beam. The center amplitude of the emission beam depends on the quantum yield, ϕ_f, of the fluorescent system

$$I_0' = \phi_f I_0 \quad (2)$$

and the intensity of the light emitted from the fluorescent system, P_{out}, is given by[8]

$$P_{out}(t) = \frac{1}{\tau}\int_{-\infty}^{t} I_0'[1 + \alpha \sin(\omega t')] \exp\left[\frac{-(t-t')}{\tau}\right] dt' \quad (3)$$

where τ is the fluorescence decay time and t' is the time at which the light was coupled into the cavity. Integration of eq 3 results in

$$P_{out}(t) = I_0'\left\{1 + \frac{\alpha}{1+\omega^2\tau^2}[\sin(\omega t) - \omega\tau \cos(\omega t)]\right\} \quad (4)$$

and rearranging eq 4 to a single sine function using the trigonometric identity derived in Appendix A leads to

$$P_{out}(t) = I_0'\left\{1 + \frac{\alpha}{\sqrt{1+\omega^2\tau^2}} \sin[\omega t - \tan^{-1}(\omega\tau)]\right\} \quad (5)$$

By comparing eq 5 to the original intensity from eq 1, a phase shift, φ, is developed between the incident and emitted light

$$\varphi = -\tan^{-1}(\omega\tau) \quad (6)$$

By measuring the phase-shift angle, the fluorescence decay time can be determined using eq 6. This method provides an indirect way to measure transient fluorescent decay, which is especially important when time-resolved measurements are impossible due to technological limitations.

2.2. Phase Shift in CRDS. A schematic diagram of a typical CRDS system is shown in Figure 1, where an optical cavity is composed of two parallel mirrors with high reflectivity. The input light beam is coupled into the cavity through the front mirror,

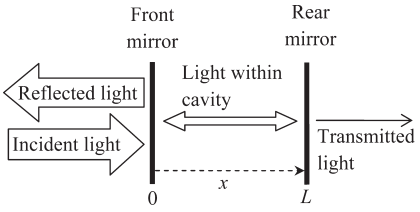

Figure 1. A schematic diagram of a typical cavity ring-down experiment.

where it is reflected back and forth within the cavity. A photomultiplier tube or similar optical detector located after the rear mirror detects the light exiting from the cavity. For convenience of discussion, a one-dimensional coordinate system will be used with the origin placed at the front mirror.

In PS-CRDS, the incident light beam is modulated at an angular frequency of ω. The light inside of the cavity undergoes multiple reflections, causing a phase shift to develop between the transmitted light and the incident light. In addition, the intensity drops due to reflection and chemical absorption losses. Because of similarities in inherent damping, pumping, and detection methods, equations derived for phase-shift fluorescence have been adapted to PS-CRDS without modification.

Although elegant, we discovered that the set of equations described previously for fluorescence are insufficient for describing the optical behavior displayed in PS-CRDS under some circumstances. Specifically, these equations were developed to describe the decay time of a fluorescent sample on a plate or in a vial, essentially representing a point in space with a negligible spatial distribution. As such, these equations do not account for (1) phase shifts induced by a long traveling distance caused by multiple reflections and (2) the myriad of overlapping waves found within a PS-CRDS cavity. In order to accurately model PS-CRDS and determine the ring-down time, it is necessary to take both of these factors into consideration. In comparison to fluorescence studies, light in a PS-CRDS system must travel not only in a temporal domain but also in a spatial domain due to the significant numbers of reflections that occur.

For a linear cavity with a length L, a wave modulated at an angular frequency ω with a velocity c (the speed of light in the cavity media) originating from the front mirror will be reflected back by the rear mirror and reflected again by the front mirror. When returning to the point of origin, a phase shift of $2\omega L/c$ results. To illustrate the superposition of waves within an optical cavity, the first few waves inside of a cavity are drawn schematically in Figure 2. In this figure, P_0 is the transmitted portion of the incident beam which propagates to the right, P_0' is the reflection of P_0 due to the rear mirror, and P_1 is the first reflected right-propagating beam. The amplitude decrease due to optical losses is neglected in Figure 2, but it is included in a later derivation of the equation. Due to the distance traveled, P_1 develops a phase difference of $2\omega L/c$ relative to P_0.

In comparison to the general waveform given by eq 1, a full traveling wave equation must be used to address the spatial changes inside of the cavity. The intensity of the pumping beam is

$$P_{in}(t,x) = I_0\left[1 + \alpha \sin\left(-\omega t + \frac{\omega x}{c}\right)\right] \quad (7)$$

Because the incident beam propagates in the positive x direction, the ωt term in eq 7 has an opposite sign to that in eq 1. The

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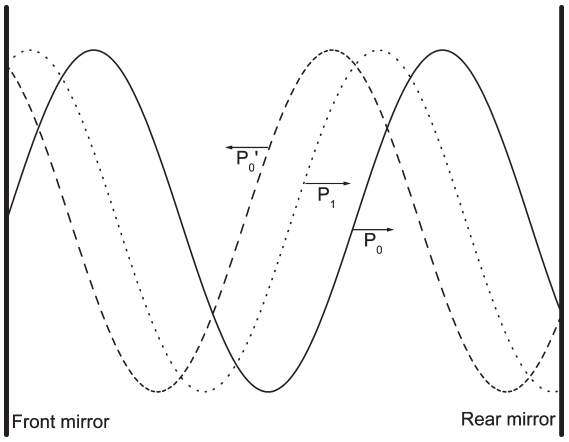

Figure 2. A schematic diagram of reflections of modulated light beams within a cavity.

intensity of the initial light beam entering the cavity can be written as

$$P_0(t,x) = I_0(1-R)\left[1+\alpha\sin\left(-\omega t+\frac{\omega x}{c}\right)\right] \quad (8)$$

where R is the reflectivity of the cavity mirrors assuming that they are identical and x $(0 \le x \le L)$ is the position within the cavity. Here, mirror reflection is assumed to be the only source of optical loss at the mirrors, and the fraction of transmitted light is equal to $(1-R)$. Considering the thin thickness of mirrors, the phase shift introduced by the mirrors is ignored. Because only waves propagating in the positive x direction (toward the right in Figures 1 and 2) will exit the cavity and reach the detector, one can ignore the waves propagating in the negative x direction. Thus, the equation for the nth $(n \ge 0)$ positive wave may be written as

$$P_n(t,x) = I_0(1-R)\left[1+\alpha\sin\left(-\omega t+\frac{\omega x}{c}+\frac{2\omega Ln}{c}\right)\right] \quad (9)$$

If each round trip of the cavity causes the signal to decay by e^{-a} due to optical losses introduced by mirror reflection, chemical absorption, and optical couplings, then eq 9 can be modified to

$$P_n(t,x) = I_0(1-R)e^{-an}\left[1+\alpha\sin\left(-\omega t+\frac{\omega x}{c}+\frac{2\omega Ln}{c}\right)\right] \quad (10)$$

The optical loss per round trip can be linked to the ring-down time of the cavity. The time that it takes light to complete a round trip within the cavity is given as

$$t_r = \frac{2L}{c} \quad (11)$$

Now, if $(1-e^{-a})$ is the loss per round trip of the cavity and the ring-down time, τ, is the time to decay to e^{-1} of the original intensity, then the number of round trips, n, required for the intensity of the signal to be reduced by a factor of e is

$$n = \frac{1}{a} \quad (12)$$

and therefore, τ may be written as

$$\tau = nt_r = \frac{2L}{ac} \quad (13)$$

Collecting the following variables

$$b = \frac{2\omega L}{c} \quad (14)$$

$$u = -\omega t + \frac{\omega x}{c} \quad (15)$$

$$I_c = I_0(1-R) \quad (16)$$

allows P_n to be written simply as

$$P_n = I_c e^{-an}[1+\alpha\sin(u+bn)] \quad (17)$$

Using an infinite series equation derived in Appendix B,[16] the sum of all of the reflected waves propagating in the positive x direction can be expressed as

$$S = \sum_{n=0}^{\infty} P_n = \frac{I_c\alpha e^a[e^a\sin(u)+\sin(b-u)]}{e^{2a}-2e^a\cos(b)+1} + \frac{I_c}{1-e^{-a}} \quad (18)$$

In eq 18, the wave intensities are added noncoherently. In PS-CRDS, the modulation wavelength is usually much longer than the cavity length; therefore, stationary interference cannot be formed. For long cavities, there are numerous cavity modes inside of the cavities. Hence, a quasi-continuous intensity distribution can be assumed in this case. Furthermore, making a variable substitution

$$A = e^{2a} - 2e^a\cos(b) + 1 \quad (19)$$

permits eq 18 to be rewritten as

$$S = I_c\alpha\frac{e^a}{A}[e^a\sin(u)-\sin(u-b)] + \frac{I_c}{1-e^{-a}} \quad (20)$$

Using the trigonometric identity derived in Appendix C, the two sine terms in eq 20 can be combined, and S may be simplified to

$$S = I_c\alpha\frac{e^a}{\sqrt{A}}\sin\left[u+\tan^{-1}\frac{\sin(b)}{e^a-\cos(b)}\right] + \frac{I_c}{1-e^{-a}} \quad (21)$$

By comparing eq 21 with the pumping beam eq 7 at the front mirror position $(x = 0)$, the following phase shift is found

$$\varphi = \frac{\omega x}{c} + \tan^{-1}\frac{\sin(b)}{e^a-\cos(b)} \quad (22)$$

In PS-CRDS experiments, the phase shift is normally measured at the exiting end of the cavity $(x = L)$. Substituting eq 12 for a and eq 13 for b in eq 22 yields

$$\varphi = \frac{\omega L}{c} + \tan^{-1}\frac{\sin\left(\frac{2\omega L}{c}\right)}{e^{2L/\tau c}-\cos\left(\frac{2\omega L}{c}\right)} \quad (23)$$

The first term in eq 23 is the phase shift if the light only makes a single pass through the cavity. The second term represents the phase shift introduced by wave overlapping inside of the cavity.

Equation 23 may be rearranged for the ring-down time

$$\tau = \frac{2L}{c \ln\left[\cot\left(\varphi - \frac{\omega L}{c}\right)\sin\left(\frac{2\omega L}{c}\right) + \cos\left(\frac{2\omega L}{c}\right)\right]} \quad (24)$$

By combining trigonometric terms in the denominator, a simplified equation for describing the relationship between the ring-down time and the phase shift can be obtained

$$\tau = \frac{2L}{c \ln \frac{\sin\left(\varphi + \frac{\omega L}{c}\right)}{\sin\left(\varphi - \frac{\omega L}{c}\right)}} \quad (25)$$

Because the detected signal must pass through the mirror at the end of the cavity, the intensity term in eq 21 must be scaled by a factor of $(1 - R)$. Therefore, the output light beam observed by the detector is equal to

$$P_{out} = I_c\alpha(1-R)\frac{e^a}{\sqrt{A}}\sin\left[u + \tan^{-1}\frac{\sin(b)}{e^a - \cos(b)}\right] + \frac{I_c(1-R)}{1-e^{-a}} \quad (26)$$

which may be rewritten in a similar form as the input beam defined by eq 7

$$P_{out} = I_0'[1 + \alpha' \sin(-\omega t + \varphi)] \quad (27)$$

By comparison, the center amplitude of the exiting beam is

$$I_0' = \frac{I_c(1-R)}{1-e^{-a}} = \frac{I_0(1-R)^2}{1-e^{-2L/\tau c}} \quad (28)$$

while the phase shift can be determined using eq 23 or 25. The relative modulation depth of the exiting beam is reduced to

$$\alpha' = \alpha\frac{e^{2L/\tau c} - 1}{\sqrt{e^{4L/\tau c} - 2e^{2L/\tau c}\cos\left(\frac{2\omega L}{c}\right) + 1}} \quad (29)$$

New equations of the phase shift, center amplitude of modulation, and relative modulation depth have been derived specifically for PS-CRDS. While these physical quantities are independent of the cavity length in the fluorescence model, they are related to the cavity length in the new theory. This is a consequence of the spatial propagation of light inside of the cavity.

3. DISCUSSION

Equations 25, 28, and 29 allow the ring-down time of a PS-CRDS system to be related to directly measurable physical quantities, such as phase shift, center amplitude of modulation, and relative modulation depth. Although it is, in principle, possible to solve for the ring-down time using the center amplitude and the modulation depth, these variables are unsuitable in practical applications due to laser power fluctuations and the weak intensity of the transmitted light. On the other hand, lock-in amplifiers can provide phase differentiation between two electrical signals with a resolution of hundredths of a degree. Therefore, phase-shift measurements are the favored choice for CRDS spectroscopic measurements.

In CRDS techniques, the ring-down time is given by[1,15]

$$\tau = \frac{L}{c[-\ln(R) + \sum_i \varepsilon_i C_i d_i]} \quad (30)$$

where ε, C, and d are the absorption coefficient, concentration, and optical path length of the absorbing chemical species, i, respectively. By comparing eqs 30 and 25, the total absorbance of chemical species, Abs, can be expressed as

$$\text{Abs} = \sum_i \varepsilon_i C_i d_i = \ln R + \frac{1}{2}\ln\frac{\sin\left(\varphi + \frac{\omega L}{c}\right)}{\sin\left(\varphi - \frac{\omega L}{c}\right)} \quad (31)$$

Using eq 31, the concentration or absorption coefficient of the chemical species can be determined directly by measuring the phase shift.

Although conceptually similar, the equations describing fluorescence and PS-CRDS have significant differences. While the phase shift is assumed to be independent of the cavity length in the fluorescence model, the length of the cavity is predicted to affect the measured phase shift in actual PS-CRDS experiments. Nevertheless, when the length of the cavity is short, the total distance traversed by the light in the cavity is negligible, and the equation describing the ring-down time of a PS-CRDS system reduces to that of the fluorescence system, as shown in the following discussion.

Taking the limit of eq 25 as the length of the cavity goes to 0 permits comparison between the equations developed for fluorescence study and PS-CRDS. Using the l'Hopital's rule, the limit can be evaluated, which yields the negative of the fluorescence equation, eq 6

$$\lim_{L\to 0}\tau = \lim_{L\to 0}\frac{2L}{c \ln \frac{\sin\left(\varphi + \frac{\omega L}{c}\right)}{\sin\left(\varphi - \frac{\omega L}{c}\right)}} = \frac{\tan(\varphi)}{\omega} \quad (32)$$

The sign difference between eqs 32 and 6 is due to the sign difference of the ωt term between eqs 7 and 1 for incident beams. This difference can also be explained by the experimental setup and principle of the two methods. In a fluorescence system, the modulated light is held back by excited molecules to be released at a later point in time. Conversely, for a PS-CRDS system, measurements of the incident and transmitted signals are made at the same time at different locations. Therefore, with reference to the incident light beam, the light transmitted through the PS-CRDS system will develop a positive phase shift, while the light released from the fluorescence plate will develop a negative shift. The sign of phase shift is unimportant in actual PS-CRDS experiments.

Alternatively, a Taylor series expansion can be performed to further illustrate the difference between eqs 25 and 6. In eq 25, $\omega L/c$ is usually a small parameter in comparison to the phase shift, φ, and a Taylor expansion of eq 25 centered at $\omega L/c = 0$ yields

$$\omega\tau = \tan(\varphi) - \frac{2}{3\sin(2\varphi)}\left(\frac{\omega L}{c}\right)^2 + O\left(\frac{\omega L}{c}\right)^3 \quad (33)$$

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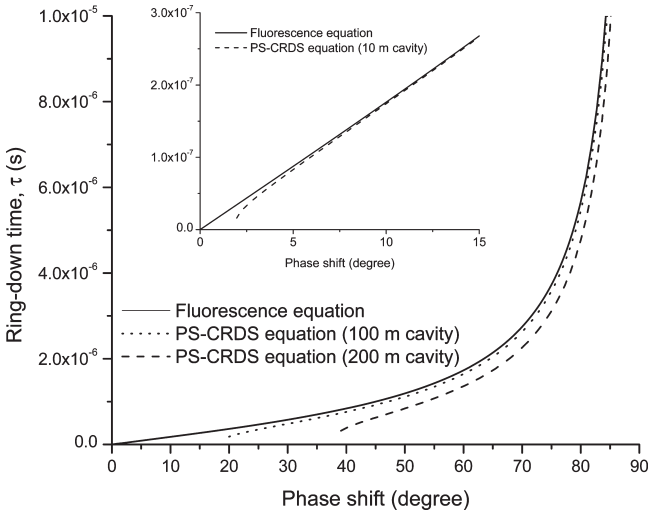

Figure 3. Comparison of ring-down times calculated using equations derived for fluorescence and PS-CRDS.

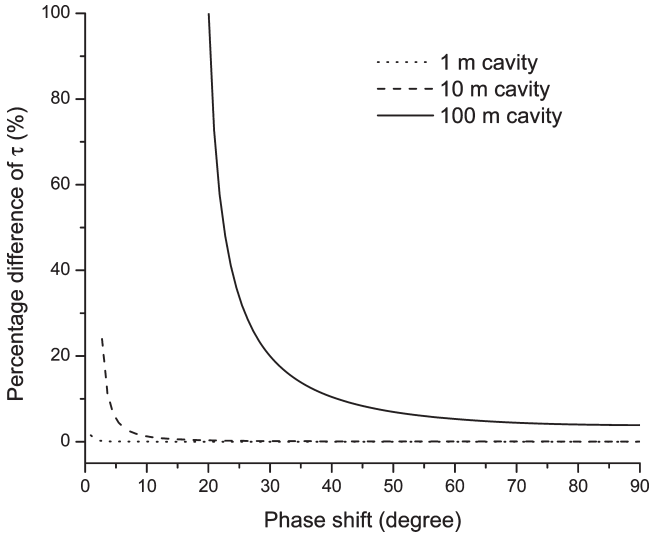

Figure 4. Percentage difference of ring-down times calculated using equations derived for fluorescence and PS-CRDS for three cavity lengths.

The first term of the Taylor series is the same as the fluorescence equation, eq 6, and the second term represents the correction resulting from our theory. In actual laboratory experiments, the phase shift is normally kept at around 45° for optimal performance of the lock-in amplifier. If δ% is chosen as the minimum for a considerable correction to the first term of the Taylor series at $\varphi = 45°$, a criterion can be derived from eq 33 for using the fluorescence equation in PS-CRDS

$$\omega L < 0.122c\sqrt{\delta} \tag{34}$$

For example, the cavity length should be less than 36 m when the light is modulated at 1×10^6 rad·s^{-1} in order to use eq 6 and remain within a 1% tolerance for accuracy. Because the angular modulation frequency, ω, and the cavity length, L, are inversely proportional, a low modulation frequency may be used to reduce the impact of a long cavity. However, changes of the modulation frequency may be limited by radio frequency interference or the capability of optical and electronic devices. For long cavities, eq 25 should be used to improve the accuracy of ring-down time determination.

In order to visualize the differences that can result between these two sets of equations, sample calculations using eq 25 have been performed assuming $\omega = 1 \times 10^6$ rad·s^{-1} and $c = 3 \times 10^8$ m·s^{-1}. The ring-down time as a function of the phase shift for three lengths of cavities is shown in Figure 3. It should be noted that the PS-CRDS plots start from a nonzero phase shift corresponding to the minimum time required for light to propagate through the cavity. This minimum phase shift is about 20° for a 100 m cavity and is proportional to the length of the cavity.

The PS-CRDS plots in Figure 3 closely resemble a tangent function as used in fluorescent studies, and the ring-down time goes to infinity when the phase shift angle approaches 90°. For short cavities, the fluorescence equations developed by F. Duschinsky provide an accurate model of the PS-CRDS system. Indeed, as shown in the inset in Figure 3, when the length of the cavity is on the order of 10 m or less, the difference between ring-down times calculated using the fluorescence and PS-CRDS models is on the order of picoseconds for small phase shifts, which is negligible for most CRDS experiments. This difference is further reduced for large phase shifts.

In conventional CRDS experiments where the cavity is formed by two mirrors in a vacuum tube, the length of cavity is usually less than 1 m. Correspondingly, the light decays so quickly due to reflections that the phase difference caused by the total propagation length becomes insignificant. In this case, the system can be modeled well using the simple tangent function developed for fluorescence studies. As the cavity length increases, however, the difference between the fluorescence and PS-CRDS equations increases exponentially.

In PS-CRDS, reduction of the speed of light is equivalent to an increase in the length of the cavity. Thus, if the cavity medium is something other than vacuum or gas, the speed of light changes due to index-of-refraction effects have to be considered. For fiber optic cavities, the cavity medium has a refractive index of about 1.5, which reduces the speed of light by approximately 33%. Consequently, a larger phase shift results, and the difference between the PS-CRDS and fluorescence equations is more pronounced for fiber optic cavities.

To better illustrate the relative difference between the fluorescence and PS-CRDS methods, the percentage difference between the two theoretical models is calculated for τ and plotted in Figure 4 for three lengths of cavities. The percentage difference is more pronounced for small phase-shift angles and approaches a constant value when the phase angle is close to 90°. As expected, the percentage difference for a 1 m cavity is too small to be observed. However, for a 100 m cavity, the percentage difference can reach more than 100% for small angles.

Given the excellent optical transmission and flexibility of modern optical fibers, CRDS techniques using optical fibers as the cavity media have been developed in the past decade. Cavities ranging in length from several meters to several kilometers have been reported.[6,10,17−20] As most of these fiber cavities are less than 100 m long, the difference between the ring-down times of the two theoretical models is generally within 100 ns and is therefore generally difficult to observe considering the uncertainty of measurements. Although uncommon, cavities longer than 1 km have been studied previously in CRDS experiments.[6,21]

Unfortunately, application of the PS-CRDS equations to these experiments could not be performed as techniques other than PS-CRDS were utilized in the experiments. It is acknowledged that experimental data are necessary to confirm the validity of the new theory. In the future, PS-CRDS experiments will be specially performed with long cavities and high modulation frequency. Results generated from these experiments will be crucial for proof of concept.

In a PS-CRDS system that contains chemical species of interest, absorption of light reduces the ring-down time and thus the measured phase shift. As indicated in Figure 3, the difference between the two theoretical models is more noticeable for small phase shift angles. For a cavity with a given length, the error associated with the old methodology increases as the molar absorptivity of the chemical species increases. However, strong absorption reduces the light intensity received by the detector, which results in unstable signals and consequently increases the uncertainty of phase angle measurements. Hence, the error of the old methodology may not be picked up easily in real absorption experiments.

4. CONCLUSION

PS-CRDS yields high-quality spectra and has been shown to be a highly efficient and low-cost alternative to pulsed CRDS. Furthermore, with the use of the equations presented in this paper, it is possible to extend the accuracy of the technique to long, flexible fiber optic cavities that are promising for applications requiring sensitive and durable fiber optic field equipment.

Phase-shift equations derived from fluorescence studies are simple and provide good accuracy for short cavities. For long cavities, the light propagation time within the cavities is too large to ignore. In this case, the fluorescence equations lose their predictive power, and the proper phase-shift equations for PS-CRDS should be used to model experimental data. In the new theoretical framework, superposition of enormous numbers of reflecting light waves within the cavity is calculated and results in a phase shift between the pumping and exiting beams. In future work, phase-shift experiments with long fiber cavities will be tested to verify the validity of the newly derived PS-CRDS equations.

APPENDIX A

Let $K = \tan\theta$
Therefore

$$\begin{aligned}\sin x \pm k\cos x &= \sin x \pm \tan\theta\cos x \\ &= \frac{1}{\cos\theta}(\sin x\cos\theta \pm \cos x\sin\theta) \\ &= \frac{1}{\cos\theta}\sin(x \pm \theta)\end{aligned}$$

As

$$\frac{1}{\cos\theta} = \sqrt{1+\tan(\theta)^2} = \sqrt{1+k^2}$$

Hence

$$\sin x \pm k\cos x = \sqrt{1+k^2}\,\sin(x \pm \tan^{-1}k)$$

APPENDIX B

$$\sum_{n=1}^{\infty} e^{-an}\sin(bn+c) = \cos(c)\sum_{n=1}^{\infty} e^{-an}\sin(bn) + \sin(c)\sum_{n=1}^{\infty} e^{-an}\cos(bn)$$

The two sums can be found in Efthimiou's work in 2006[16]

$$\sum_{n=1}^{\infty}\sin(nx)e^{-nt} = \frac{e^{-t}\sin x}{1-2\cos xe^{-t}+e^{-2t}}$$

$$\sum_{n=1}^{\infty}\cos(nx)e^{-nt} = \frac{e^{-t}(\cos x - e^{-t})}{1-2\cos xe^{-t}+e^{-2t}}$$

Substitution of these two equations yields

$$\begin{aligned}&\sum_{n=1}^{\infty} e^{-an}\sin(bn+c) \\ &\quad= \frac{e^a\cos(c)\sin(b)+e^a\sin(c)[\cos(b)-e^{-a}]}{e^{2a}-2e^a\cos(b)+1} \\ &\quad= \frac{e^a[\cos(c)\sin(b)+\sin(c)\cos(b)]-\sin(c)}{e^{2a}-2e^a\cos(b)+1} \\ &\quad= \frac{e^a\sin(b+c)-\sin(c)}{e^{2a}-2e^a\cos(b)+1}\end{aligned}$$

Then

$$\begin{aligned}&\sum_{n=0}^{\infty} e^{-an}\sin(bn+c) \\ &\quad= \sin(c)+\sum_{n=1}^{\infty} e^{-an}\sin(bn+c) \\ &\quad= \sin(c)+\frac{e^a\sin(b+c)-\sin(c)}{e^{2a}-2e^a\cos(b)+1} \\ &\quad= \frac{e^a[e^a\sin(c)-2\sin(c)\cos(b)+\sin(b+c)]}{e^{2a}-2e^a\cos(b)+1} \\ &\quad= \frac{e^a[e^a\sin(c)-\sin(c)\cos(b)+\sin(b)\cos(c)]}{e^{2a}-2e^a\cos(b)+1} \\ &\quad= \frac{e^a[e^a\sin(c)+\sin(b-c)]}{e^{2a}-2e^a\cos(b)+1}\end{aligned}$$

APPENDIX C

$$\begin{aligned}&k\sin x \pm \sin(x-x_0) \\ &\quad= k\sin x \pm \sin x\cos x_0 \mp \cos x\sin x_0 \\ &\quad= (k\pm\cos x_0)\sin x \mp \cos x\sin x_0 \\ &\quad= (k\pm\cos x_0)\left(\sin x \mp \frac{\sin x_0}{k\pm\cos x_0}\cos x\right)\end{aligned}$$

Let

$$k' = \frac{\sin x_0}{k\pm\cos x_0}$$

Then

$$k\sin x \pm \sin(x-x_0) = (k\pm\cos x_0)(\sin x \mp k'\cos x)$$

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Using Appendix A

$$= (k \pm \cos x_0)[\sqrt{1 + k'^2}\, \sin(x \mp \tan^{-1} k')]$$

$$= (k \pm \cos x_0)\left\{\sqrt{1 + \left(\frac{\sin x_0}{k \pm \cos x_0}\right)^2}\, \sin\left[x \mp \tan^{-1}\left(\frac{\sin x_0}{k \pm \cos x_0}\right)\right]\right\}$$

$$= \sqrt{k^2 \pm 2k \cos x_0 + 1}\, \sin\left[x \mp \tan^{-1}\left(\frac{\sin x_0}{k \pm \cos x_0}\right)\right]$$

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