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Effect of Laser Lineshape on the Quantitative Analysis of Cavity Ring-Down Signals

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Abstract—In cavity ring-down spectroscopy (CRDS) the finite spectral width of the laser pulse leads to a ring-down signal in which the decay is not strictly exponential. Nevertheless, the simple assumption of a single-exponential form is the method used in almost all analyses. This paper provides a generalized treatment of the errors introduced by such an approach. We re-examine the equations governing the ring-down signals and show that the problem may be parameterized with two dimensionless variables: the laser linewidth normalized by the absorption linewidth, and the peak sample absorbance normalized by the empty cavity loss. For different values of these two parameters, we simulate multi-exponential ring-down signals and the errors introduced by fitting them with single-exponential signal profiles. We examine the validity of analyzing CRDS data assuming a single-exponential form, both with an uncorrected and an effective absorption lineshape. We show that the effective lineshape is rigorously correct in the early-time (or weak-absorption) limit, and that for a peak based analysis, it gives better results than the uncorrected lineshape in all cases. We find that analysis using the area is comparably robust to analysis using the peak with an effective lineshape, and thus recommend the former, as it does not require knowledge of lineshapes. The simulations include the effects of variable time windows in the fitting procedure for both Doppler and Lorentz absorption and laser lineshapes. We find that the single-exponential approximation is increasingly valid in earlier time windows and we suggest using this approach as a means to verify the validity of quantitative absorption measurements extracted from experimental ring-down signals.

INTRODUCTION

Cavity ring-down spectroscopy (CRDS) has become a widely used method in absorption spectroscopy. Detailed descriptions of the technique have been presented elsewhere [1, 2]. The technique may be summarized as follows. A laser beam is coupled into a high finesse optical cavity containing a sample. The light inside the cavity decays (rings down) owing to cavity loss (primarily mirror losses) and sample absorptive loss. A photodetector is used to measure the ring-down signal. The signal profile as a function of time is fitted to yield the absorptive loss. Spectra may be obtained by scanning the laser wavelength. This paper concerns the effect of the laser bandwidth on the ring-down signal, and how the bandwidth influences the extraction of quantitative data from CRDS experiments.

As will be discussed in the next section, for a laser of sufficiently narrow linewidth, the temporal profile of the ring-down signal has a single-exponential form. In such cases the ring-down profile may be characterized by the 1/e time of the decay, commonly termed the ring-down time. The ring-down time is proportional to the inverse of the losses (sample and empty cavity), and may be conveniently related to the loss arising from sample absorption. As the laser linewidth becomes broader, the single-exponential model loses its validity. Different spectral components within the laser pulse are at different tunings relative to the linecenter of the absorption, and therefore decay at different exponential rates, resulting in a multi-exponential ring-down signal. Nevertheless, the assumption of a single-exponential form of the ring-down signal is valid in many cases, and its use is appealing from a practical experimental point of view. In some cases an effective absorption lineshape is assumed, with the aim of accounting for instrumental broadening by the laser. The advantages of assuming a single-exponential are that generally the laser lineshape does not need to be actively measured, and the ring-down data may be fitted in a comparatively easy manner, often in real time. This method is used in the majority of current research.

In cases where the ring-down signals are well described by single-exponential decays it still may be necessary to include the laser lineshape in the data analysis [3–5]. Typically, an experimentalist measures a spectrum of ring-down time versus wavelength, and then directly converts this information to a spectrum of absorbance versus wavelength. Subsequent analysis, for example to obtain concentration, is typically based on either the peak or integrated area of the measured absorbance lineshape. In the case of an analysis based on the measured peak absorbance, an effective lineshape is sometimes used to account for instrumental broadening of the spectrum arising from the laser linewidth. The effective lineshape is defined as the convolution of the original absorption lineshape with the laser lineshape. The role of the effective lineshape has been discussed before (e.g., [3]), and will be further addressed here. When reading CRDS papers, care must be taken to understand whether the effective lineshape was used implicitly. The use of the effective lineshape is very analogous to the approach used in conventional absorption spectroscopy (and LIF); however, we show that it is not rigorously correct in CRDS. Another approach is to base the analysis on the wavelength-integrated area of a CRDS feature, by computing what sample concentration would yield the same area. In this case assuming an effective lineshape makes no difference because it gives the same area. The computations presented in this paper are intended to clarify the appropriate use of these methods.

A number of studies have reported departures from single-exponential ring-down signals, and different methods of data collection and signal fitting have been implemented [5–11]. Van Zee *et al.* [6] recognized that under a single-exponential assumption, lasers of different line-widths gave different apparent absorptive losses (or concentrations) for the same transition under the same conditions. These authors demonstrated that the correct values could be obtained by actively monitoring the laser linewidth, and using it as a parameter in the data fitting procedure. Mercier *et al.* [10] and Jongma *et al.* [5] collected data assuming a single-exponential form and then corrected the resulting absorbances based on a time-averaged measurement of the laser linewidth. Furthermore, it has been recognized that in cases where non-exponential effects are important, the portion of the temporal decay (or time window) used in fitting the data influences the resulting absorbance [6, 8, 9]. These studies have found that earlier time windows result in higher apparent absorbances than later time windows.

This paper examines the effect of laser linewidth on the quantitative analysis of CRDS data for cases where the cavity transmission profile may be neglected. In particular, we explore the range of validity, and errors induced by making a single-exponential approximation. We show that the problem may be described with two dimensionless parameters: (1) the laser linewidth normalized by the absorption linewidth, and (2) the peak sample absorbance per pass normalized by the empty cavity loss per pass. We simulate multi-exponential ring-down signals and the errors induced by fitting single-exponential forms to those signals. Based on theory and the simulation results, we suggest strategies for handling the laser lineshape in CRDS data analysis.

THEORY

We concern ourselves with the case of time-averaged, pulsed laser measurements using free-running ring-down cavities. Then, with sufficient averaging, the effects of the cavity transmission profile (i.e., etaloning) may be neglected. Because of the drift in the physical length of the cavity (or laser frequency), the laser has a different tuning relative to the cavity's spectral profile on each shot. These tunings are effectively random and serve to wash out the effects of the cavity transmission profile. For example, for a 1 m length cavity operating at 500 nm, displacements of 125 nm are sufficient to shift the tuning by half a free spectral range. Also, in many experiments the laser lineshape is broad relative to the cavity free spectral range, and/or multiple transverse modes are excited. Both of these effects diminish the role of the cavity transmission profile. Experimentally, repeatable spectra imply that cavity effects have been removed by averaging and hence may be neglected. From the superposition principle, the effect of sufficient averaging on the ring-down signal is equivalent to assuming the cavity transmission profile is constant (flat). Because we are not concerned here with the absolute magnitude of the ring-down signals, we may neglect this constant. If we assume that mode beating may be neglected, and for simplicity we assume that the sample absorption coefficient has no spatial or temporal dependence, then the temporal dependence of the ring-down signal S may be described by (adapted from Zalicki and Zare [3])

$$S(t, \nu_L) = S_0 \exp\left[-\frac{tc(1-R)}{l}\right] \times \int_{-\infty}^{+\infty} d\nu L(\nu-\nu_L) \exp\left[-\frac{tck(\nu)l_{\mathrm{abs}}}{l}\right], \qquad (1)$$

where c is the speed of light, l is the cavity length, $1 - R$ is the effective empty cavity losses (including mirrors and any scattering) on a single pass through the cavity, ν_L is the detuning of the laser from the transition line-center, $L(\nu)$ is the laser lineshape (centered at zero and normalized in frequency space), $k(\nu)$ is the absorption coefficient (centered at zero and in units of per length), and l_{abs} is the column length of the absorber. The expression represents a sum of exponentials with different decay rates, corresponding to different tunings relative to the absorption, weighted by the laser lineshape. The exponential factor in front of the integral represents the empty cavity decay, which we assume to have no spectral dependence.

For the case of a laser with a very narrow linewidth in comparison to the absorption linewidth, the laser lineshape function may be approximated as a delta function. In this case the multi-exponential expression (1) reduces to the familiar single-exponential form:

$$\lim_{L(\nu) \to \delta(\nu)} S(t) = S_0 \exp[-t/\tau] \qquad (2a)$$

$$1/\tau = \frac{c}{l}(k(\nu_L)l_{\mathrm{abs}} + (1-R)) \qquad (2b)$$

where we define the ring-down time τ, as the $1/e$ time of the exponential decay. It is also useful to define an empty cavity ring-down time $\tau_0 = c(1 - R)/l$, corresponding to the $1/e$ time found in the absence of the absorber (or with the laser detuned).

We find another limiting case of expression (1) by preserving the laser linewidth but considering the limit of early time. When the argument of the second exponential in Eq. (1) is small, one obtains the following limit:

$$\lim_{t \ll \frac{l}{ckl_{abs}}} S(t) = S_0 \exp[-t/\tau], \quad (3a)$$

$$1/\tau = \frac{c}{l}[l_{abs} k_{\mathrm{Eff}}(\nu_L) + (1-R)],$$

$$k_{\mathrm{Eff}}(\nu_L) = \int_{-\infty}^{+\infty} d\nu L(\nu - \nu_L) k(\nu). \quad (3b)$$

In this early time (or weakly absorbing) limit, the signal again reduces to a single-exponential but with an effective absorption lineshape.

In cases where the ring-down signal is assumed to have a single-exponential form (with or without the effective lineshape) it is straightforward to determine the apparent absorbance per pass, *Abs*, from the ring-down time and the empty-cavity ring-down time. In practice the empty cavity ring-down time may be found by removing the sample or by completely detuning the laser. We can rearrange Eqs. (2b) or (3b) as

$$Abs = \frac{l}{c}\left[\frac{1}{\tau} - \frac{1}{\tau_0}\right], \quad (4)$$

where $Abs \equiv kl_{\mathrm{abs}}$ if the uncorrected lineshape is assumed, and $Abs \equiv k_{\mathrm{eff}} l_{\mathrm{abs}}$ if the effective lineshape is used.

It is useful to define a dimensionless parameter, $\kappa \equiv k(0)l_{\mathrm{abs}}/(1-R) \equiv AbsPeak/(1-R)$, as the peak absorbance per pass normalized by the empty cavity loss per pass. The limiting condition for early-time in Eq. (3) may be rewritten as $t \ll \tau_0/\kappa$. Note that owing to the empty cavity decay, the largest times of interest are on the order of several τ_0. For example, using temporal fitting windows that extend to 10% of the initial amplitude of the ring-down signal corresponds to $t \le 2.3\tau_0$. Therefore, in cases with weak normalized sample absorption for which $\kappa \ll 1$, the ring-down signal is given by expression (3) for all times of interest. In such cases, the ring-down signal has a single-exponential form, but with an effective lineshape. The effective lineshape is defined as the convolution of the absorption lineshape with the laser lineshape. The effective lineshapes (or overlap integral) is commonly used in conventional absorption spectroscopy and LIF. Note that in conventional absorption and LIF the use of the effective lineshape is rigorously correct, whereas in CRDS the assumption of a single-exponential form with an effective lineshape is rigorously correct only in the early-time limit (which also may be thought of as a weak absorption limit).

We show how to recast the problem in dimensionless variables. In many cases the absorption is due to a spectral feature that may be characterized by its linewidth, $\mathrm{FWHM_{Abs}}$, and its peak absorbance *AbsPeak*. Note that the transition strength, and wavelength-integrated area of the absorbing feature, are both proportional to the product of the peak (*AbsPeak*) and width ($\mathrm{FWHM_{Abs}}$). The laser lineshape is characterized by its full width at half maximum, $\mathrm{FWHM_{Laser}}$, so that we may define a dimensionless parameter, $\Delta \equiv \mathrm{FWHM_{Laser}}/\mathrm{FWHM_{Abs}}$, as the laser linewidth normalized by the absorption linewidth. The remaining dimensionless parameters required to define the problem are the peak sample absorbance per pass normalized by the cavity losses per pass, $\kappa \equiv AbsPeak/(1-R)$; dimensionless time, $t' \equiv tc(1-R)/l$; and dimensionless frequency, $\nu' \equiv \nu_L/\mathrm{FWHM_{Laser}}$. The expression (1) for the multi-exponential ring-down signal may be rewritten in terms of only these variables as

$$S(t', \nu', \Delta, \kappa)$$
$$= S_0 \int_{-\infty}^{+\infty} d\nu^* \frac{1}{\Delta} f_1\left(\frac{\nu^*}{\Delta}\right) \exp[-t'[1 + \kappa f_2(\nu^* + \nu'\Delta)]], \quad (5a)$$

where we redefine the integration variable as $\nu^* \equiv (\nu - \nu_L)/\mathrm{FWHM_{Abs}}$, and we have adopted generalized (and dimensionless) lineshape functions defined as

$$f_1(x) \equiv \mathrm{FWHM_{Laser}} L(x\mathrm{FWHM_{Laser}}),$$
$$f_2(x) = \frac{l_{\mathrm{abs}}}{AbsPeak} k(x\mathrm{FWHM_{Abs}}), \quad (5b)$$

where we again use *AbsPeak* as the peak absorbance ($AbsPeak \equiv k(0)l_{\mathrm{abs}}$). Both lineshapes are centered at zero, and $L(\nu)$ is normalized in frequency space. We do not consider specific times and frequencies (except $\nu' = 0$); hence, all ring-down experiments governed by the multi-exponential expression (1) may be characterized by the two dimensionless parameters Δ and κ.

SIMULATION

To examine the effects of laser lineshape on quantitative measurements we simulate the ring-down signals given by the general expression (1), or equivalently Eq. (4). We are interested in understanding the validity of the single-exponential approximation, and therefore we simulate the results of fitting the full ring-down signals with single-exponential profiles. By comparing apparent values derived from the single-exponential fits to actual values computed from the original absorption parameters we compute the errors induced by using the single-exponential approximations (2) and (3).

In Figs. 1 and 2 we examine the errors introduced into the analysis of CRDS signals if one assumes a single-exponential decay and uses the peak of the measured CRDS feature. In Fig. 1 we simulate an analysis that assumes the CRDS lineshape is the same as the

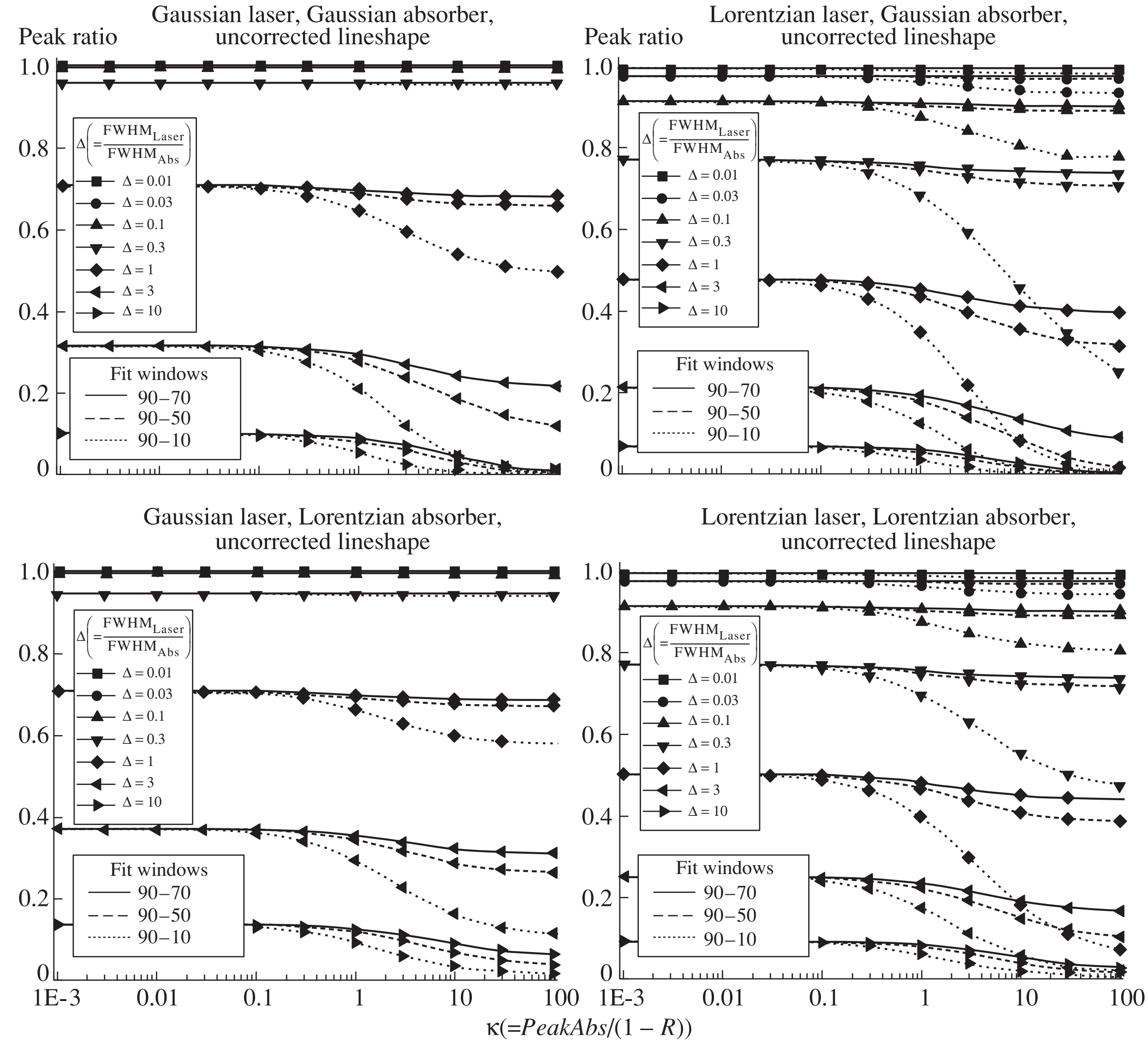

Fig. 1. Shows plots of the ratio of apparent peak absorbance to actual peak absorbance, if the uncorrected absorption lineshape is assumed. The apparent peak absorbance is found from single-exponential fits of simulated ring-down signals. The graphs are plotted as a function of the normalized absorption strength κ, and are plotted for different values of the normalized laser linewidth Δ, different fitting windows, and different combinations of Gaussian and Lorentzian laser and absorption lineshapes.

original (uncorrected) lineshape, whereas in Fig. 2 we simulate an analysis that assumes an effective (corrected) lineshape. For different combinations of the dimensionless parameters Δ and κ we simulate the corresponding multi-exponential ring-down signal using (1), and then compute the result of fitting a single-exponential to that signal. (In order to replicate common experimental technique, we perform a least squares linear fit to the logarithm of the signal.) The single-exponentials are fitted for ring-down times, which are converted to values of apparent absorbance using Eq. (4). In Fig. 1 we plot the ratio of the apparent peak absorbance found in this manner to the actual peak computed from the original absorption lineshape. In Fig. 2 we compute the ratio of the same apparent peak absorbances found from the exponential fits, but now to the peak absorbance computed from the effective lineshape. The ratios in both figures are plotted as a function of the normalized absorption strength, κ. The error induced by assuming a single-exponential form with the corresponding lineshape, and performing a peak analysis is, therefore, unity minus this ratio. In each figure, the four graphs are for the different combinations of Gaussian and Lorentzian laser and absorption lineshapes. Each graph contains seven families of curves. Each family corresponds to a different value of the laser linewidth parameter Δ, while the three curves in each family correspond to different fitting windows. The fitting windows describe the portion of the ring-down signal used in the single-exponential fit. For example, a window of 90–50 means that the single-exponential fit to the ring-down signal used the portion of the ring-

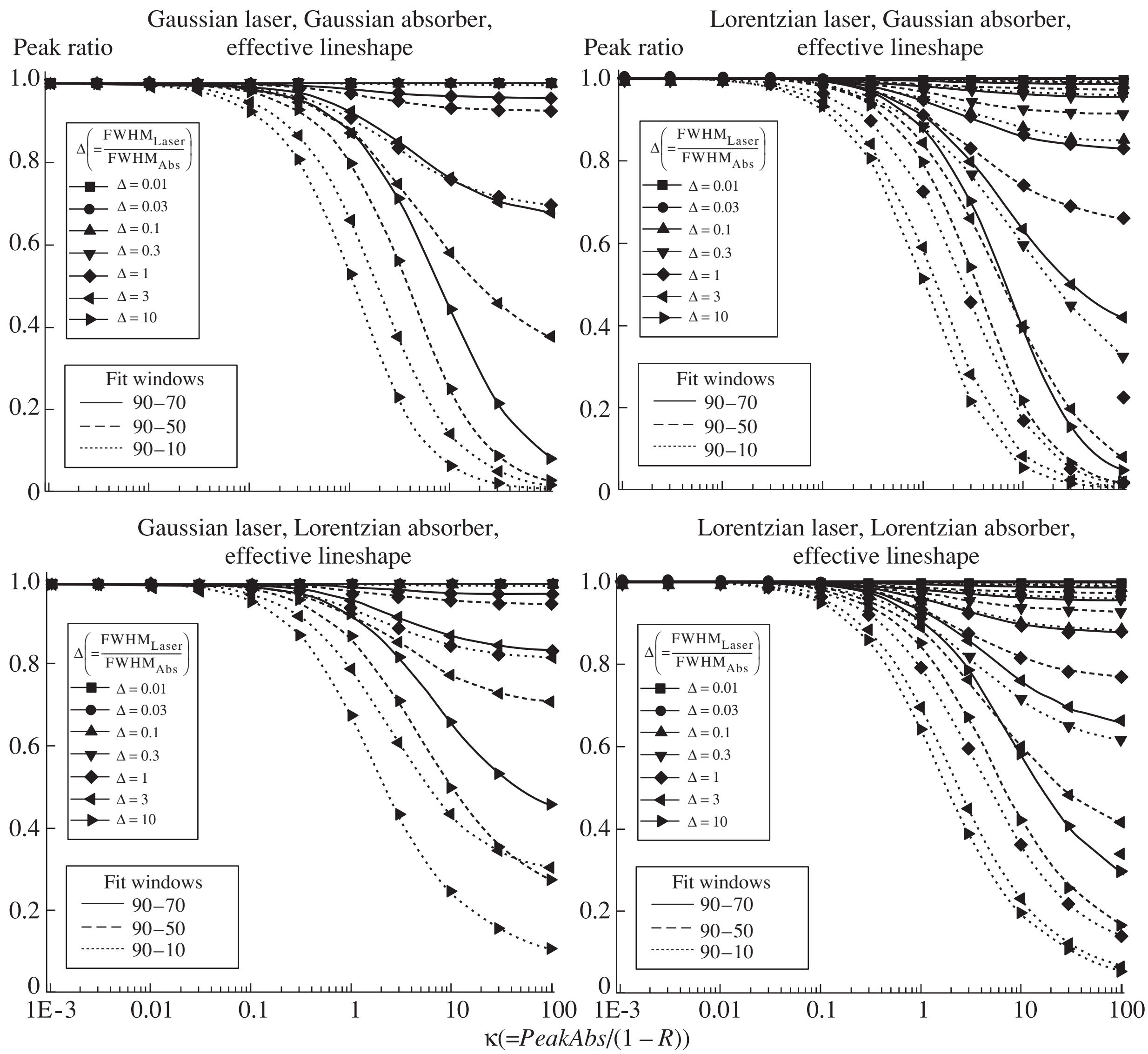

Fig. 2. Shows plots of the ratio of apparent peak absorbance to actual peak absorbance, if the effective absorption lineshape is assumed. The effective absorption lineshape is defined as the convolution of laser lineshape with absorption lineshape. The apparent peak absorbance is found from single-exponential fits of simulated ring-down signals. The graphs are plotted as a function of the normalized absorption strength κ, and are plotted for different values of the normalized laser linewidth Δ, different fitting windows, and different combinations of Gaussian and Lorentzian laser and absorption lineshapes.

down between 90% of its maximum (initial) amplitude and 50% of its initial (maximum) amplitude. These windows are dynamic; the corresponding times vary with laser tuning and parameter values. We have selected three fitting windows: 90–70, 90–50, and 90–10. The selection of the 90% point is motivated by the fact that it is experimentally difficult to use the data in the very early portion of the ring-down signal because of the presence of transients and elastic scatter.

In Fig. 3 we examine the errors introduced into the analysis of the CRDS signals if one assumes single-exponential decays and uses the area of the measured CRDS feature. Again, for different combinations of the dimensionless parameters Δ and κ we simulate the multi-exponential ring-down signals. We emulate an analysis in which the laser is scanned over the absorption lineshape and the measurement is based on the integrated area. We do not account for error due to finite laser step-size. At each laser wavelength we compute the apparent absorbance found from a single-exponential fit to the multi-exponential signal. We then integrate these absorbance values over wavelength to obtain an apparent area. We plot the ratio of the apparent area found in this manner, to the actual area computed from the original lineshape. (Note that the actual (uncorrected) and effective lineshapes have the same area by definition, and therefore assuming a single-exponential with either one leads to the same ratio of areas.) We plot the ratios for different values of normalized laser line-

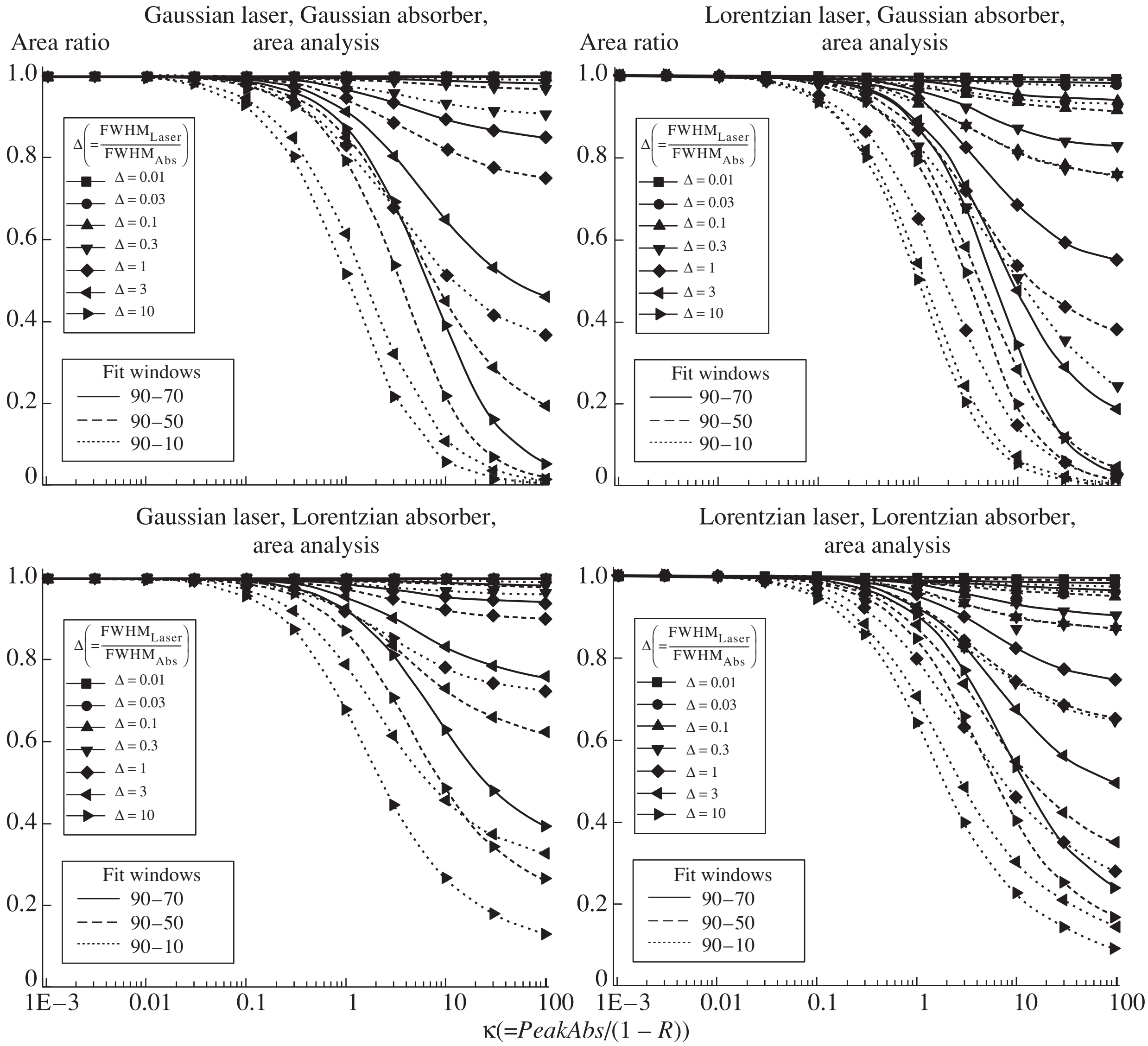

Fig. 3. Shows plots of the ratio of apparent absorbance area to actual absorbance area. Apparent absorbances are found from single-exponential fits of simulated ring-down signals. These absorbances are then integrated by wavelength over a spectral feature in order to yield an apparent area. The graphs are plotted as a function of the normalized absorption strength κ, and are plotted for different values of the normalized laser linewidth Δ, different fitting windows, and different combinations of Gaussian and Lorentzian laser and absorption lineshapes. (Uncorrected and effective lineshapes have the same area, so either may be used.)

width, and different fitting windows, as a function of the normalized absorption strength.

In order to help orient the reader, we explicitly describe the contents of one of the plots—we select the Gaussian–Gaussian graph in Fig. 1. In all plots, for a given time window, the ratio of apparent peak to actual peak (or apparent area to actual area) decreases as the laser bandwidth parameter increases. Similarly, for a given laser bandwidth parameter, the ratio decreases as the time window becomes longer. It is easiest to identify the curves by starting from the bottom of each plot. In each case the lowest curve corresponds to the 90–10 time window, and a normalized laser bandwidth of 10. For example, in the Gaussian–Gaussian case in Fig. 1, for a normalized sample absorption κ = 1, the Δ = 10 and 90–10 window measurement would have an apparent peak absorbance equal to 0.05 of the actual peak absorbance. At the same conditions, the 90–50 window would have a peak ratio of 0.08, and the 90–70 fit-window would have a peak ratio of 0.09. The next curve (moving up the figure) is for a normalized laser bandwidth Δ = 3, a window of 90–10, and for a normalized sample absorption κ = 1, gives a peak ratio of 0.21. And so on. For the curves in Figs. 2 and 3 there is some crossover. (For example, in the Gaussian–Gaussian plot in Fig. 2, the 90–10 curve for normalized laser bandwidth $\Delta = 3$ is below the 90–50 curve for normalized laser bandwidth $\Delta = 10$.) However the 2 conditions stated above remain valid.

DISCUSSION

The graphs presented in Figs. 1–3 allow an assessment of the errors arising from a single-exponential approximation to the full multi-exponential ring-down signals. Theoretically, we expect departures from single-exponential behavior to increase as either Δ (the laser linewidth normalized by the absorption linewidth) increases, or κ (the sample absorption normalized by the empty cavity loss per pass) increases. This behavior is borne out in the simulations. Clearly, therefore, to operate in regimes that are well modeled by single-exponential ring-down profiles, narrow laser linewidths are preferable, as well as appropriately chosen mirror reflectivities. The departure arising from laser linewidth is more intuitive, and more widely recognized in the literature. For a given absorber, a progressively wider laser linewidth samples an increasingly larger portion of the absorption lineshape, and the signal rings-down with an increasing range of decay rates. Therefore the ring-down signal becomes increasingly multi-exponential. The departure arising from large values of the normalized sample absorption is expected from Eq. (3) and may be explained as follows. As sample absorption loss increases relative to the cavity loss, the light resonant with the sample decays away more quickly compared to the light further from the sample resonance. Thus the more resonant light has a decreasing contribution to the ring-down signal at later times. In other words, the fit is effectively biased toward laser frequencies that are further from the sample resonance, particularly at later times. Consequently the treatment yields apparent absorption losses that are too low. For a sufficiently wide laser and sufficiently strong absorber this type of analysis leads to a form of "saturation" where the resonant ring-down signals are essentially the same as the empty-cavity ring-down signals, and the single-exponential assumption leads to nearly zero apparent losses. This type of saturation effect has been discussed by Meijer *et al.* [5]. Note that this effect is independent of laser energy and should not be confused with bleaching-type saturation that occurs when the laser fluence is high enough to saturate the transition itself [9, 11].

We expect from Eq. (3) that for appropriate conditions, the peak found assuming a single-exponential form with the effective lineshape will track the actual effective peak very well. For example, Fig. 2 shows that for a Gaussian laser lineshape, a Gaussian absorber lineshape, and a 90–50 fit, the peak found in this way has ~0.2% error for $\Delta = 1$, and $\kappa = 0.1$. Under the same conditions, the peak found assuming a single-exponential form with the actual lineshape has an error of ~30%. The discrepancy is simply a result of the instrumental broadening by the laser. Similar to conventional absorption, the laser lineshape causes a broadening of the CRDS lineshape, and an associated reduction in the peak. Performing a peak analysis using the actual lineshape rather than the effective lineshape is similar to performing a conventional absorption measurement without correcting for the effective lineshape (or overlap integral). If the laser broadening is neglected systematically low results are obtained. Figure 2 shows that a peak-based analysis with the effective lineshape is well justified over a large parameter space. As we expect, the approximation holds better for small Δ, small κ, and shorter windows. As mentioned, some authors have used the effective lineshape implicitly, and care must be taken when reading the CRDS literature to understand the method of data analysis. Therefore, for analyses based on the peak of the measured spectrum the effective lineshape method is clearly preferable. A drawback of this approach is that it requires knowledge of both the laser and absorber lineshape and is sensitive to errors from either. In contrast, an analysis based on the wavelength-integrated area of the absorption feature does not need detailed knowledge of either the absorption or laser lineshapes. Comparison of Figs. 2 and 3 shows that an analysis based on the area of the absorbing feature is comparably robust to a peak analysis (with the effective lineshape). Therefore, we suggest that when possible an analysis using the integrated area of the CRDS feature is the preferred method of quantification. In order to simulate (predict) the shape of experimental spectra, a "guess" at the effective lineshape may be used.

In all cases, the results of the simulation show that under the single-exponential approximation better results are obtained from the earlier time window, as expected from Eq. (3), and as observed in experiments [6, 8, 9]. In fact for any experimental conditions we can theoretically find a sufficiently short, and early-time window in which the ring-down signals are well modeled by the single-exponential with the effective lineshape. However, experimentally it is difficult to work with very short windows because the signal-to-noise ratio drops, and it is difficult to work in the very early portion of the ring-down signal because of interference from elastic scatter and transients. The simulation results suggest a method to vary the time windows to verify measurements. In all cases where the apparent losses are low compared to the actual losses, shorter time windows increase the apparent losses. Therefore, if the experimenter verifies that the same apparent losses are found with shorter windows, then the experimenter has verified that the apparent losses are indeed the actual losses. Also, we notice that in strongly absorbing cases where the single-exponential errors tend to be larger, experiments tend to have larger signal-to-noise ratios, and therefore it may be possible to use shorter time windows.

The simulation results give insight into the dynamic range limitations of the CRDS technique. At conditions where the single-exponential approximation loses its validity, linearity is lost, and dynamic range is compromised. Bear in mind that the experimenter has essentially three free parameters, the dimensionless laser linewidth, the dimensionless absorption strength, and the fitting window. Figures 2 and 3 show that for reasonably narrow lasers a large dynamic range may be achieved if we extend toward the weak absorption direction (low κ), since ratios of apparent to actual absorbance remain near unity. Conversely, extending toward stronger absorptions (high κ) results in a loss of linearity due to laser bandwidth effects (the approximation in (3) is violated). For example, for a laser with a normalized Gaussian linewidth of $\Delta = 1$, a Gaussian absorber linewidth, and a 90–50 fit, an area analysis has less than 1% departure from linearity for all values of the normalized absorption strength κ less than ~1. If desired, one can always obtain smaller κ by using lower reflectivity mirrors. If the absorber is too strong CRDS may not be the optimal method. The trade-off is that signal-to-noise ratio tends to drop for absorbers with small dimensionless absorption strengths (κ), because the variation in ring-down times is small. Similarly, shorter windows improve dynamic range but reduce the signal-to-noise ratio. The use of a narrower laser linewidth is always a means to improve the dynamic range because higher dimensionless absorption strengths are tolerated before non-linearities are introduced. If multi-exponential decays can not be avoided several approaches have been demonstrated. The treatments by Mercier *et al.* [10] and Jongma *et al.* [5] correct for laser bandwidth effects by using modeling results like those in this paper. Van Zee *et al.* [6] have actively measured the laser lineshape and used it in a multi-exponential fit. If possible, however, it is preferable to find experimental conditions that yield (nearly) single-exponential signals.

CONCLUSION

This paper examines the effect of laser lineshape on the quantitative analysis of CRDS data for cases where the cavity transmission profile may be neglected, m particular, we explore the range of validity, and errors induced by making a single-exponential approximation. We show that the problem may be described with two dimensionless parameters: (1) the laser linewidth normalized by the absorption linewidth, and (2) the peak sample absorbance per pass normalized by the empty cavity loss per pass. As either of these parameters increase in magnitude, multi-exponential effects become more pronounced. We simulate multi-exponential ring-down signals and the errors induced by fitting single-exponential forms to those signals. The simulations show that for sufficiently early time-windows, sufficiently narrow laser linewidths and sufficiently weak absorbers, the signals may be accurately described with a single-exponential form using the effective lineshape. On the other hand, we find that peak based analyses using the actual lineshape systematically give low apparent absorbance because instrumental broadening of the CRDS lineshape by the laser is not accounted for. We suggest that an alternative to using a peak based analysis (with an effective lineshape), it to use an analysis based on the area of the spectral feature. The latter approach has the distinct advantage that neither the absorber lineshape nor the laser lineshape must be well known, and its accuracy is comparable. We show that progressively earlier (and shorter) temporal windows give better results under single-exponential approximations, and suggest this as a means to verify measurements. The results in this paper give a convenient means for researchers to assess the role of laser lineshape in their own experiments, and may guide the selection of the method used for data analysis.

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