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Noise caused by a finite extinction ratio of the light modulator in CW cavity ring-down spectroscopy

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Abstract A model is presented for the effect of a finite extinction ratio of the light modulator used in continuous wave cavity ring-down spectroscopy (CW-CRDS) experiments. We present a simple analytical expression for the minimum isolation required to prevent a significant increase in the fluctuations of the cavity decay rate, which determine the sensitivity of the method. We also present systematic measurements of the signal to noise in CW-CRDS as a function of the effective isolation of the light modulator, and excellent agreement with the model is found.

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1 Introduction

Starting from the introduction of cavity ring-down spectroscopy (CRDS) [1], it has become a widely used method for trace detection [2–4] and weak transition measurement [1, 5]. In CRDS, absorption and scattering loss of a sample placed inside a high-finesse optical cavity is determined by an increase in the decay rate of light intensity trapped inside the cavity. Sensitivities to loss as small as 10^{-9}–10^{-11} cm^{-1} are routinely obtained in the visible and near IR, where the highest reflectivity dielectric mirrors are available. The highest sensitivities are usually realized by using a narrow bandwidth continuous wave laser to excite the cavity and then observing the cavity decay by rapidly (compared to the cavity storage time) switching off the input radiation, which is known as CW-CRDS [6, 7]. This method gives a more reproducible excitation of a single mode of the cavity, thus minimizing fluctuations caused by, among other reasons, spatial variations in the mirror reflectivity. Despite the great success of the method, very few CRDS experiments have reached the fundamental detection limit, which is limited by shot noise in the observed cavity intensity during the decay [5, 8]. The reasons for the higher than predicted noise are not fully understood, though there are several established contributions, including detector noise, mirror loss drift, and modulations in cavity decay rate caused by even extremely weak back coupling of light leaving any of the ports of the cavity [9]. In this paper, we will quantitatively examine an additional potential noise source which has not been explicitly analyzed previously—the effect of a finite extinction ratio of the intensity modulator used to interrupt excitation of the cavity.

Qualitatively, the effect of incomplete shut-off of the excitation laser is easy to understand. The residual optical power couples into the excited mode. Since the optical coherence time of most lasers is less than the CRDS cavity storage time, this extra field adds with random phase and creates an interference noise on the decay. Thus, if the decay has a power signal-to-noise ratio of $N:1$, one could anticipate that a minimum extinction ratio of $N:1$ for the optical field and thus $N^2:1$ for the optical intensity is needed for the remaining noise field not to cause a noise in the cavity decay rate larger than the shot and detector noise. While this provides a rough estimate, the reality (as will be demonstrated below) is more complex, since the detector and shot-noise contributions have noise correlation times much shorter than the cavity decay time constant but the net intracavity noise field generated by a finite modulator extinction coefficient has a correlation time equal to that of the cavity. In this work, we will present a simple analytical

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expression for the excess noise induced by a finite extinction coefficient that properly accounts (in the linear noise approximation) for the temporal correlations of the noise.

We are not aware of any previous quantitative measurements of CW-CRDS sensitivity as a function of the effective modulator extinction ratio. We have modified the RF drive of our acousto-optic modulator (AOM) to allow a controlled extinction ratio of the cavity excitation laser. Using this system, we have recorded ensembles of cavity decays (attempting to hold all other conditions constant) and determined the variance of the cavity decay rates of the ensemble as a function of effective modulation extinction ratio. The results are in excellent agreement with our analytical model.

Following this introduction, we will first present the noise model giving the analytical form of the fluctuations of the decay rate by this light leakage. Then, we will explain the details of our experimental setup. The experimental results are compared with the prediction by the model with further discussions. After the conclusions and acknowledgments, the appendix contains the derivations of some noise correlation functions and the averaged transmission waveforms considering the frequency sweep of the laser and its line width.

2 The model

Consider a linear optical cavity made from two mirrors with power reflectivity R and transmission T separated by length L. The cavity will have free spectral range FSR $= c/2L$, where c is the speed of light inside the medium between the mirrors (which we will assume is negligibly different from that in vacuum). Without an intracavity sample, the intracavity light intensity will decay at rate $k = c(1-R)/L$ with lifetime $\tau = 1/k$ [10]. We consider excitation of the cavity by a single-mode laser with Lorentzian spectral shape with frequency full width at half-maximum (FWHM) $\Delta\nu_L$. Such a line shape is appropriate for the widely used semiconductor diode lasers where the line width arises from fast phase modulation of the laser intracavity light, leading to phase diffusion [11]. In the appendix, we analyze the transmission of a low-loss optical cavity including the effects of laser phase diffusion. If the center laser frequency is held on the center of a cavity mode and we assume perfect mode matching of the input radiation to that mode, the time-averaged steady-state transmission of the cavity is shown to be given by [3]

$$T_c = \left(\frac{T}{1-R}\right)^2 \frac{1}{1+2\pi\tau\Delta\nu_L} \xrightarrow{\Delta\nu_L\tau\gg1} \left(\frac{T^2}{1-R}\right)\frac{c}{2\pi\Delta\nu_L L}, \tag{1}$$

where $\Delta\nu_L\tau \gg 1$ implies that the correlation time of the input radiation, $(\pi\Delta\nu_L)^{-1}$, is much shorter than the cavity decay time, τ. For a more complex cavity, with more than two mirrors, the same expression applies for the transmission, but with L as the round trip optical path length, R^2 the product of the reflectivity for each reflector and the transmission coefficient for each intracavity optic in one round trip, and T^2 replaced by the product of the transmissions of the input and output cavity optics. For the case of a lossy sample inside the cavity, let α be the sum of absorption and scattering coefficients of the medium between the mirrors, which we will assume to change slowly over the width of a given cavity mode. In this case, the above expression for cavity transmission holds with the change $1-R \to 1-R\exp(-\alpha L) \approx 1-R+\alpha L$, since we assume that both $1-R$ and $\alpha L \ll 1$. For the case of a spatially dependent absorption coefficient, $\alpha L \to \int \alpha(z)\,\mathrm{d}z$, where the integration is over a single pass or a round trip of the cavity depending on whether the single pass or round trip R is used.

The above expression gives the mean transmission but, for input by a laser with $\Delta\nu_L\tau \gg 1$, there will be considerable fluctuations. In this case, the input is injecting radiation into the cavity with a phase which fluctuates rapidly compared to the cavity storage time [12]. By the central limit theorem, the cavity output field will have Gaussian random real and imaginary amplitudes and the output intensity will follow a χ^2 in two degrees of freedom distribution [3], which is $P(I_t(t)) = \exp(-I_t(t)/I_0)/I_0$, where $I_0 = \langle I_t(t)\rangle$ is T_c times the incident optical power. $I_t(t)$ is the transmitted intensity. We used $\langle\cdots\rangle$ to represent quantities averaged over the noise. Expressing the output field of the cavity as the sum over all possible numbers of round trips (each weighted by the appropriate power of R), it is shown in the appendix that for $\Delta\nu_L\tau \gg 1$ the cavity transmission intensity fluctuations follow a simple exponential law as for a low-pass filter:

$$\big\langle\big(I_t(t)-I_0\big)\big(I_t(t')-I_0\big)\big\rangle = I_0^2\exp\big(-|t-t'|/\tau\big).$$

We now consider a typical CW-CRDS experiment where the transmitted power of the cell is monitored and the input laser greatly attenuated once the transmitted power reaches some threshold, I_{th}. Obviously, I_{th} must not be more than a few times I_0 or the rate at which this happens would be quite low, hurting the detection rate. If the input laser is completely eliminated, the intracavity light intensity and the power on the detector will decay exponentially in time with time constant τ. However, if the input light is attenuated by an inverse power extinction ratio $\epsilon_r \ll 1$, then the field already present in the cavity when the input laser is attenuated will decay with time constant 2τ but there will also be a weak input of radiation, generating a field with random phase relative to the initial value. The light output intensity will display beating between these waves, generating noise in the decay and thus fluctuations in the resulting fit to the cavity decay rate k (or equivalently τ). We use the square root of intensity as a convenient unit for the field amplitude. We take $t = 0$ to be the time at which the light intensity is attenuated, corrected for the minimum propagation delay to the detector. At $t = 0$, the field on the detector is $\sqrt{I_{\text{th}}}$. Summing over the light field amplitudes from the laser that entered the cavity at different times after the attenuation, it is easy to demonstrate that the noise field on the detector, $\delta E(t)$, generated by post-attenuation input has the following statistical property: $\langle \delta E(t)^* \cdot \delta E(t+\delta t)\rangle = \exp(-k\delta t/2)[1-\exp(-kt/2)]\epsilon_{\text{r}} I_0$. The $[1-\exp(-kt/2)]$ term arises from the build up of the noise field inside the cavity and the $\exp(-k\delta t/2)$ term arises from the correlation time of the intracavity noise field due to the input of the field with rapidly changing phase. When we add this noise field to the decaying field injected into the cavity prior to attenuation of the laser, we find that the beating produces an intensity noise on the detector, $\delta I_t(t)$, with the following correlation function: $\langle \delta I_t(t) \cdot \delta I_t(t+\delta t)\rangle = \exp(-k(t+\delta t)[1-\exp(-kt)]2\epsilon_{\text{r}} I_0 I_{\text{th}}$. (We have neglected terms proportional to ϵ_{r}^2.) This noise has a maximum at $t = \ln(2)/k$ (i.e. the half-life of the exponential decay) and has a noise spectrum very similar to the signal itself. Note that we do not consider the field stored in the cavity at $t = 0$ to be a noise field even though it was generated by a similar input of radiation with short coherence time. This is our signal that would give a pure exponential decay in the limit of complete modulation, $\epsilon_{\text{r}} \to 0$.

Consider that the ring-down intensity is captured as N points by a digitizer with rate of $(\Delta t)^{-1}$. In order to maximize signal to noise in the extracted decay rate, we want to work in the limits $k\Delta t \ll 1$ and $Nk\Delta t \gg 1$. Physically, this means that we observe many points per decay time and we fit the ring-down signal far into the tail. Let $a = \exp(-k\Delta t)$. We first consider the case where each point in the cavity decay is equally weighted, as is appropriate for the case where detector noise dominates. From the nonlinear least squares fitting equations to an exponential decay we previously presented [8], it can be shown that the rate of change in decay rate due to noise at point i is given by

$$\left(\frac{\partial k}{\partial I_i}\right) = \frac{(1-a^2)^2}{a^2 I_{\text{th}}\Delta t}\left[a^{i-2} - (1-a^2)\mathrm{i}a^{i-4}\right]. \tag{2}$$

We are primarily interested in k because the sample absorption coefficient and thus the sensitivity of CRDS is calculated from $\Delta k/c$, where Δk is the change in cavity decay rate caused by introduction of the sample into the optical cavity. Thus, the standard error in the estimated absorption coefficient is directly proportional to the standard error in the value of k extracted from the data. Error propagation (and considerable algebra) gives for the variance in the fitted cavity decay rate

$$\sigma^2(k) = \sum_{i,j}\left(\frac{\partial k}{\partial I_i}\right)\langle \delta I_t(t_i)\cdot \delta I_t(t_j)\rangle\left(\frac{\partial k}{\partial I_j}\right)$$

$$\xrightarrow{Nk\Delta t\gg 1} \frac{2(a^2-a+1)(1-a^2)^5}{(1-a^3)^3\Delta t^2}\epsilon_{\text{r}} I_0/I_{\text{th}}$$

$$\xrightarrow{k\Delta t\ll 1} \frac{64}{27}k^2\epsilon_{\text{r}} I_0/I_{\text{th}}. \tag{3}$$

As anticipated by the simple argument given in the introduction, the fractional noise in k is proportional to $\sqrt{\epsilon_{\text{r}}}$ with a proportionality constant on the order of unity. This is the noise in k determined from a single decay. If the signals from N_{d} decays are averaged, or the k value from each decay averaged, the expected noise in k should decrease as $1/\sqrt{N_{\text{d}}}$ as long as the cavity loss remains stable in time.

This noise in the extracted cavity decay rate can be compared to the variance in k caused by detector noise that we earlier derived [8],

$$\sigma^2(k) = 8k^3\Delta t(\sigma_{\text{d}}/I_{\text{th}})^2, \tag{4}$$

where σ_{d} is the root mean square (RMS) detector noise in power units as measured by the A/D converter. If we take, as representative of our CW-CRDS experiments, $k\Delta t = 0.01$ and an initial signal to noise of 1000:1 on the decay (i.e. $\sigma_{\text{d}}/I_{\text{th}} = 10^{-3}$), we see that without excitation laser leakage through the modulator (i.e. $\epsilon_{\text{r}} = 0$) the fractional noise of k is 0.028% (on a single shot). If we take $I_{\text{th}} = 2.5 I_0$ (for which numerical simulations predict that a mean time to trigger after the laser is applied to the cavity is 6.2τ), the noise in k caused by finite ϵ_{r} will be $\sim\sqrt{\epsilon_{\text{r}}} = 0.031\%$ with $\epsilon_{\text{r}} = 1\times 10^{-7}$. Thus, for these parameters, a ~50% increase in the RMS noise of the experiment is predicted.

If the ring-down transient is fitted with shot-noise appropriate weighting (i.e. each point given a weight inversely proportional to its fitted value) [8], then $\partial k/\partial I_i$ changes and we obtain modified results for the extinction ratio induced noise in the determined cavity decay rate:

$$\frac{\partial k}{\partial I_i} = \frac{(1-a)^2}{a I_{\text{th}}\Delta t}\left[a - (1-a)\mathrm{i}\right], \tag{5}$$

$$\sigma^2(k) \xrightarrow{Nk\Delta t\gg 1} \left(\frac{2(1-a)^2(3a^3+3a^2+3a-1)}{a(1+a)^2}\right)\epsilon_{\text{r}} I_0/I_{\text{th}}$$

$$\xrightarrow{k\Delta t\ll 1} 4k^2\epsilon_{\text{r}} I_0/I_{\text{th}}. \tag{6}$$

For shot noise limited data, appropriately weighted, the predicted noise in the decay rate is $k^3\Delta t(\sigma_0/I_{\text{th}})^2$ [8], where σ_0 is the noise at the beginning of the decay. Thus, in this case, for the same initial signal-to-noise ratio, one requires an extinction ratio more than one order of magnitude higher (27/2, i.e. an additional 11.3 dB) than for the detector noise limited case to prevent light-leakage noise from dominating over the noise with an ideal light intensity modulator.

The above analysis assumes that the center wavelength of the laser stays exactly on resonance with the cavity mode throughout the decay. In most experiments, the cavity or the laser is swept onto resonance. However, to maximize the build up of intensity in the cavity modes (and thus to achieve an optimized signal to noise) for a monochromatic laser, the scanning rate should satisfy $s = \mathrm{d}\nu/\mathrm{d}t \ll (2\pi\tau^2)^{-1}$, which means that the relative shift of the frequency of the cavity mode and the laser during one cavity lifetime should be much less than the width of the cavity mode. In this limit, the frequency shift will have little effect on noise generated by the leaking radiation. For $\tau = 221$ μs, this rate is about 3.3 MHz per second, an impractically slow sweep rate if one sweeps the full free spectral range of the cavity (which is typically several hundred MHz). For the more commonly encountered case where the laser line width is much greater than the cavity resonance, the maximum scan rate can be increased since the maximum build up of the field is decreased by the short coherence time of the laser. In the appendix, we present an analytical expression for the mean cavity transmission for this case, which is found to be a function of a reduced sweep rate $\beta = 2\pi s/(Dk)$, with modest reduction in peak transmission for $|\beta| < 1$. Here, $D = \pi\Delta\nu_L$ is the inverse of the laser field correlation time.

3 Experimental setup

In this work, we used a slightly modified version of a working CW-CRDS instrument that we have previously described [3]. As such, we will describe it only briefly, focusing on what has been changed (see Fig. 1). Our setup is similar to other CW-CRDS instruments, including those in commercial trace-gas analyzers such as those of Tiger Optics, Inc. We use a cavity formed from two highly reflective mirrors (from ATFilms) that had a design center coating wavelength of 1540 nm, one flat and one with 1-m radius of curvature, separated by 39.5 cm. The decay time constant of the empty cavity is about 221 μs near 1512 nm, corresponding to a mirror loss of 6 ppm per reflection. The flat mirror is mounted on a plate that can be moved by three PZT actuators. Light from a fiber-coupled distributed feedback (DFB) laser is converted to free-space propagation, passes through an optical isolator, and then an AOM. The first diffraction order of the AOM is mode matched to the optical cavity through the flat mirror. The cavity length is modulated by applying a 15 Hz triangle wave to the PZTs with sufficient amplitude to scan slightly over one FSR of the cavity (379.5 MHz), which insures that the laser and cavity will come into resonance at least once in each modulation half-cycle. When the laser power transmitted through the ring-down cavity reaches the preset threshold, a home-built comparator generates a trigger pulse signal, which is used to rapidly turn off the input laser and trigger the data acquisition by a 12-bit A/D card digitizing at 1 MHz to record the single exponential decay signal for 2 ms. Each ring-down decay is fitted with a nonlinear weighted least squares fit to an exponential decay plus a baseline.

In order to adjust the residual RF power level when the AOM is off, we add two microwave switches (Mini-Circuits, ZYSW-2-50DR), one 20 dB attenuator (Mini-Circuits, VAT-20), and one 0–69 dB step attenuator (Weischel Eng., AF117-69-02-01) between the 80 MHz RF oscillator and the RF amplifier (with gain 35.6 dB), connected as

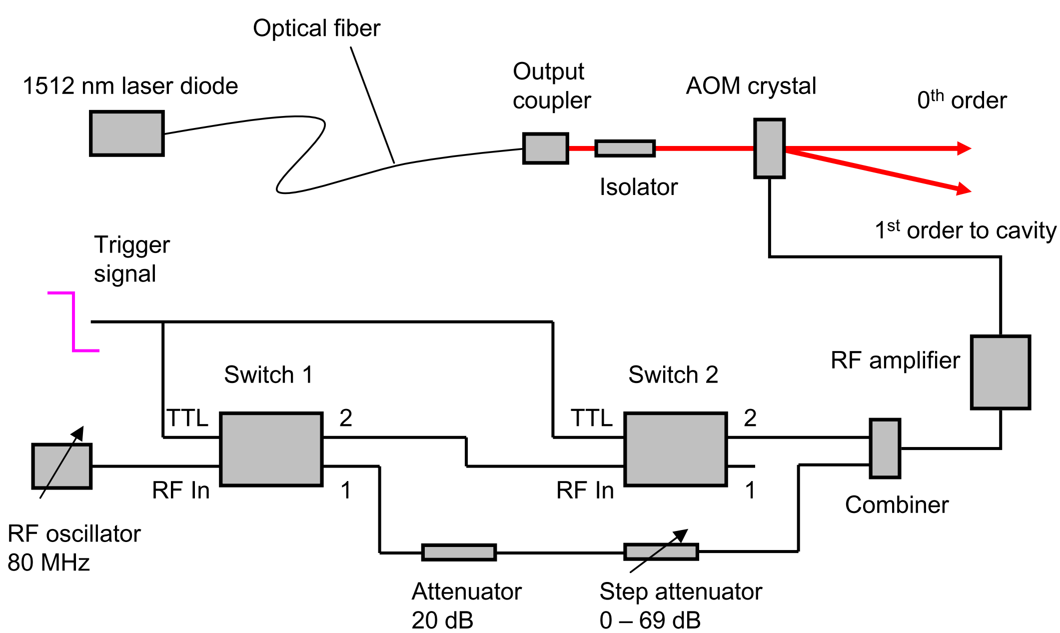


Fig. 1 AOM as the light switch in CW-CRDS with controlled extinction ratio

in Fig. 1. The trigger signal is used to control both switches, changing the RF path. When the trigger signal is high, the output 2 of both switches is on while the output 1 is off. The RF power from the oscillator will pass through both switches and be coupled to the AOM after amplification (ON channel). When the trigger signal is low, the RF power from the oscillator will pass through two attenuators before it becomes amplified and coupled to the AOM (OFF channel). The RF power to the AOM when it is off can be adjusted by the step attenuator. The ON and OFF channels are put together by a combiner (Mini-Circuits, ZSC-2-1). Both microwave switches have response time on the scale of tens of ns. The incident light can be shut off by the AOM in less than 1 µs. The RF extinction ratio of both the ON and OFF channels (when it is at −89 dB attenuation) is measured separately to be larger than 73 dB, limited by the noise level of the oscilloscope. Optical extinction is measured by putting a detector before the cavity and apertured down to approximately the laser beam diameter at this point. However, the measured optical extinction ratio of the AOM is only 53 dB when the OFF channel is set to −89 dB attenuation. This light leakage is due to light scattered by optical elements of the system. Even when the AOM is disconnected from the RF amplifier, the same amount of scattered light is measured by the detector and will disappear only when the incident laser is turned off completely. After we removed the AOM from the system, the scattered light intensity was reduced by about 70%, demonstrating that the AOM crystal is itself the dominant source of scattering. The laser frequency of the first-order diffraction is shifted by 80 MHz from the input while the scattered light has the unshifted laser frequency when the AOM RF is off. This suggests that any beating frequency due to this scattered light in the ring-down signal should be at 80 MHz. However, our detector amplifier includes one low-pass RC filter with 3 dB frequency of ∼300 kHz, which removes such high-frequency beating. In addition, the unshifted radiation is not resonant with a cavity mode and thus has very low transmission.

The total RF power loss caused by both microwave switches and the combiner is about 2.4 dB, which reduces the maximum output RF power from 1 W to about 0.6 W. This is less than 0.85 W, the power corresponding to the maximum efficiency (∼85%) of the first-order diffraction. The loss of light power in the first-order diffraction can be compensated by increasing the laser current correspondingly. In our experiments, the laser power reaching the cavity is about 2 mW. We have selected the laser wavelength to avoid the strong absorption due to atmospheric water vapor.

4 Results and discussion

In order to test our model for the effect of a finite light modulator extinction ratio on CW-CRDS sensitivity, we measured the quantity $(\sigma_k/k)^2$ for about 400 recorded decays for different attenuation levels of the OFF channel in the AOM driver from 20 to 89 dB with steps of 5 dB. Here, σ_k is the standard deviation of the ensemble of 400 decays and k is the averaged decay rate of the ensemble. We first established that above the level where scattered light is significant (see above) the light intensity was linear in RF power; thus, the dB of RF attenuation reflects an equivalent dB of optical power attenuation. The actual RF attenuation at 80 MHz was determined for each attenuator and for each setting of the variable attenuator. For each attenuation level, two different measurements were performed. One is under the normal condition of a length-modulated cavity, leading to an effective linear frequency sweep of cavity modes relative to the incident laser of 11.4 GHz/s. For the other measurement, the PZTs were not scanned. The resonance between the laser and the cavity is achieved by manually tuning the DC control voltage of the PZTs very slowly until the laser is on resonance with the cavity modes. In this situation, the relative frequency sweeping speed between them is very small, determined by a low (∼Hz) frequency jittering of the diode laser. The laser can be regarded as always on resonance with the cavity in the measurement, as described in Sect. 2. Figure 2 plots the results of these measurements. Equation (3) predicts a straight line in a log–log plot of $(\sigma_k/k)^2$ vs. the extinction ratio, as proved by Fig. 2. With the PZTs not scanned, data with the extinction ratio less than 75 dB can be fitted to the solid line that corresponds to (3) with $I_{\mathrm{th}} = 1.5I_0$ very well. With the PZTs scanned, data with the extinction ratio less than 65 dB can still be fitted to a straight line (the dotted one). The results show that, for the same AOM extinction ratio, the noise level in k when the cavity is swept is less than that when the cavity is not scanned. Qualitatively, this is because the frequency sweeping brings the laser out of resonance faster with the remaining laser power in the cavity, leading to less leakage power coupled into the cavity and hence less noise in k even with a smaller trigger threshold (by a factor of three) for the sweeping situation. The time required for the cavity mode to shift by the half-width at half-maximum (HWHM) of the short term laser diode spectral width (∼1 MHz) is ∼90 µs, much less than one cavity decay time. Unfortunately, the analytical calculation for $(\sigma_k/k)^2$ when the cavity mode or the laser frequency is swept if one includes the finite laser line width in the calculation is very numerically demanding, involving several six-nested integrals of a rapidly oscillating integrand (see the appendix). We have used (23) in the appendix to simulate the frequency-sweeping situation. Our simulation reproduced the dotted line in the figure perfectly. For data points with extinction ratio less than 75 dB (non-sweeping) and 65 dB (sweeping), we found excellent agreement between the model and experiments. From Fig. 2, we can see that the decrease of $(\sigma_k/k)^2$ when the extinction ratio increases

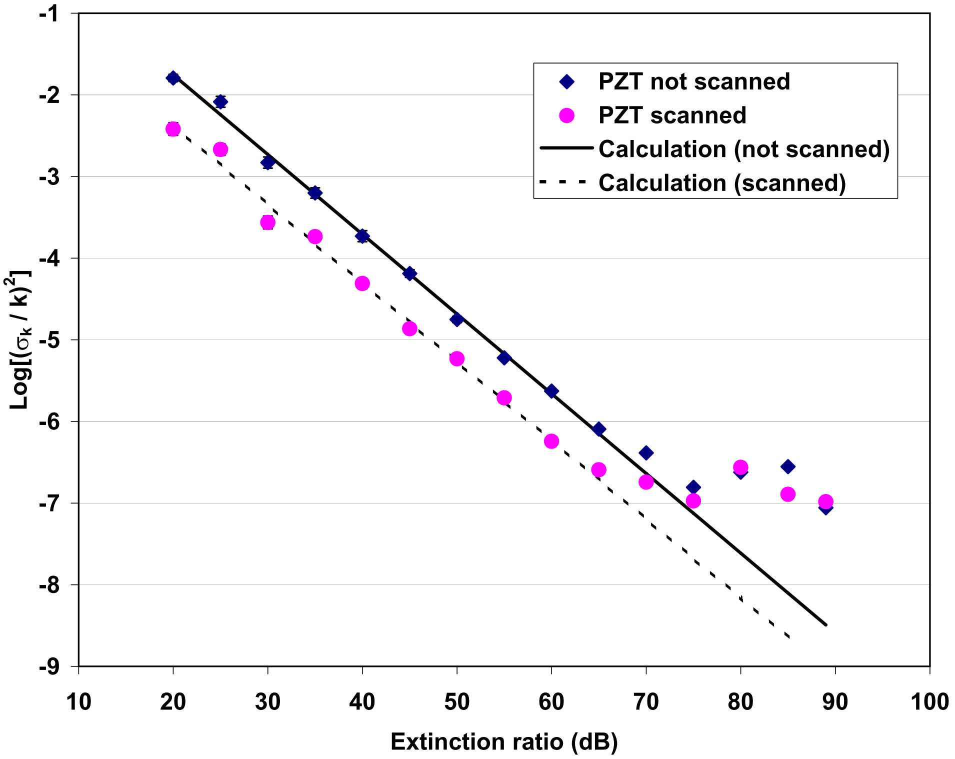


Fig. 2 $(\sigma_k/k)^2$ vs. the extinction ratio of the AOM switch. k is the averaged decay rate of the ensemble of 400 decays and σ_k is the standard deviation of the ensemble

reaches a limit at some point. For extinction ratios larger than this value, the sensitivity of our CW-CRDS is limited by detector noise and cavity drift. The observed noise floor is $\sigma_k/k \sim 5 \times 10^{-4}$. In the experiment, the signal-to-noise ratio is about 1500. Thus, the ideal limit of σ_k/k, predicted by (4), is $\sim 1.3 \times 10^{-4}$ if the detector noise is the only noise source in the system.

When the light leakage induced noise dominates, we expect the reduced χ^2 of our fits of the cavity decays to a single exponential to be substantially larger than 1, as the detector noise is determined far in the tail of the decay where the light-leakage noise has decayed to an unobservable level. Figure 3 shows one example of the residuals of the fit, recorded with the extinction ratio of 20 dB. The noise level is much higher than the detector noise. Also, the noise at the beginning of the decay caused by the light leakage is higher than that at the tail of the decay. Figure 4 shows the noise power spectrum of the fit residues, averaged over 50 decays with reduced $\chi^2 > 1.5$, observed both with and without a frequency sweep. In both cases, an extinction ratio of 20 dB was used. Both noise spectra have approximately a Lorentzian shape with HWHM of 6 and 13 kHz, respectively, and are significantly larger than the cavity mode width (which has FWHM of 723 Hz). The least-squares fit adjusts the baseline such that the zero-frequency noise component (which corresponds to a DC offset) is zero. The wider bandwidth of the frequency-swept noise spectrum likely reflects the shorter time that the noise is effectively injected into the cavity or, in another way, shows that more noise-frequency components can be coupled into the cavity because of the frequency sweeping. Also, because of the frequency sweep, the noise amplitude in the lower spectrum is less than that in the upper one, as explained above.

In our simulations, the laser line width is a critical parameter. The DFB diode laser we used has a line width of 10 MHz in a time period of seconds because of the low-frequency jittering. However, we found that the laser line width in a short time period (~ms) is much less and is about 1 MHz. We measured the laser line width by using the self-homodyne method [13]. The 11.4-μs time delay of one arm in the measurement is realized by using extra 2.4-km single-mode fiber in this arm. This delay time is much larger than the coherence time of the laser. The measured noise spectrum of the homodyne signal is not exactly Lorentzian and contains other frequency components but, between DC and 5 MHz, it can be fitted to a Lorentzian shape with HWHM of 1 MHz very well. Figure 5 shows the measurement result.

From (26) in the appendix, we noticed the following fact:

$$s\int_{-\infty}^{\infty}\langle I_t(t)\rangle \mathrm{d}t = \left(\frac{T}{1-R}\right)^2 I_L\left(\frac{k}{4}\right). \qquad (7)$$

Here, s is the frequency sweep rate (Hz/s) of the laser. This means that the product on the left is a constant independent of the laser line width. We have measured this product by recording time-averaged transmitted waveforms at several

Fig. 3 One example of fitted residual of bad decays with extinction ratio of 20 dB. The detector RMS noise level is only 2 mV. The time constant τ of this decay is about 223 μs

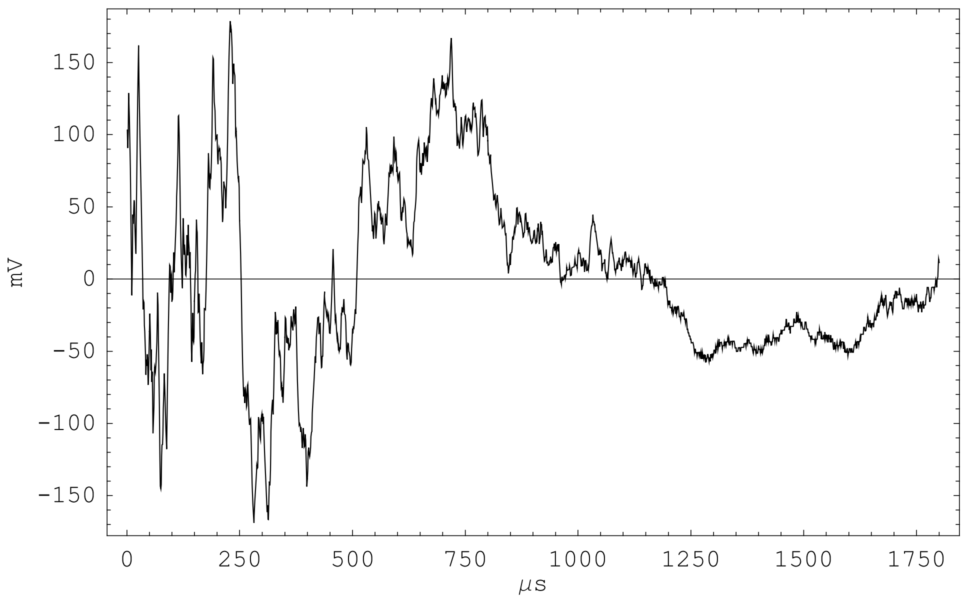
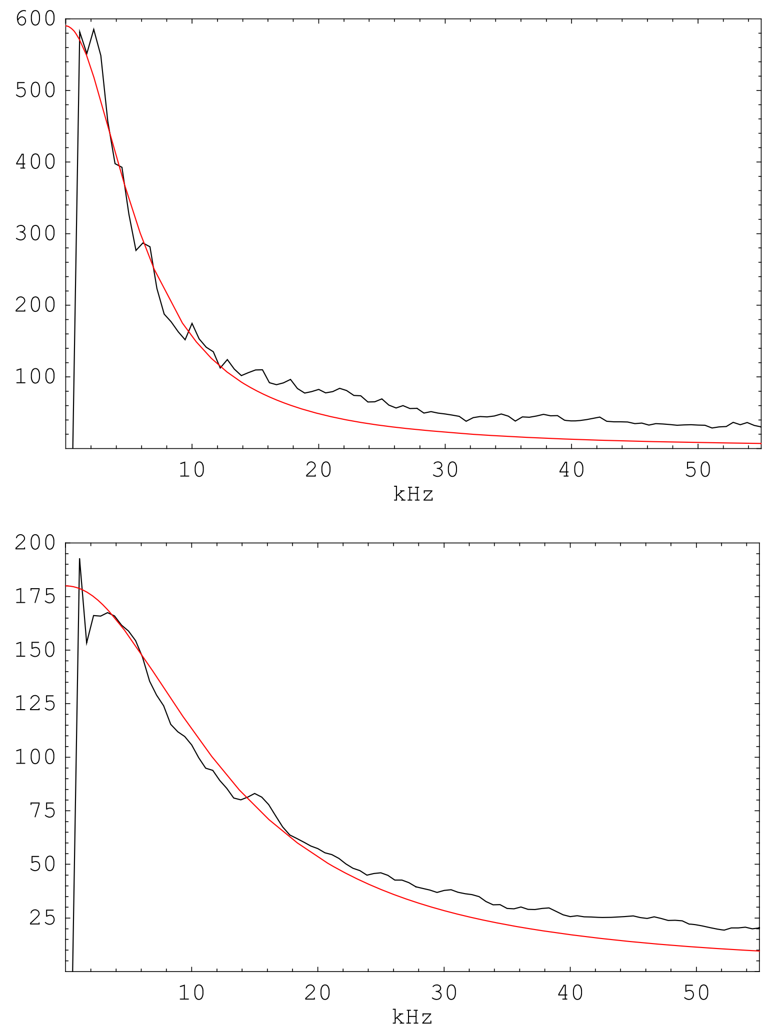


Fig. 4 Averaged noise spectra of fitted residual of decays with reduced $\chi^2 > 1.5$, recorded with an input intensity extinction ratio of 20 dB. The *upper panel* is from decays where the cavity was not intentionally swept relative to the laser while the *bottom panel* is for the case where 11.4 GHz/s linear frequency sweep was applied to the cavity. The *red curves* are fitted Lorentzian shapes. The unit of the vertical axes for both panels is arbitrary units



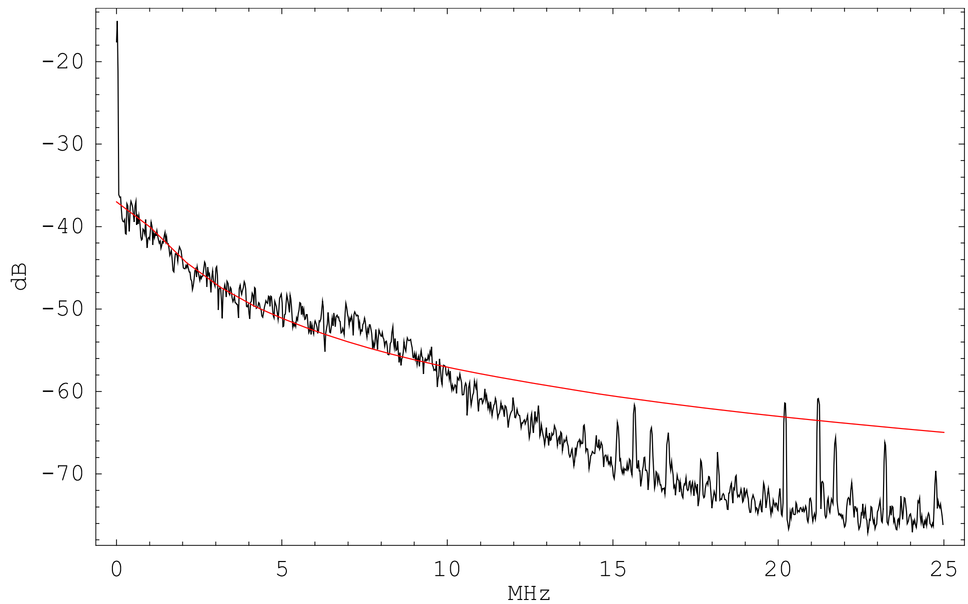


Fig. 5 Noise spectrum of the homodyne signal, averaged 25 times. The spectrum between DC and 5 MHz can be fitted to a Lorentzian (the *red curve*) with 1 MHz HWHM. The spike at zero frequency is from the DC level in the homodyne signal

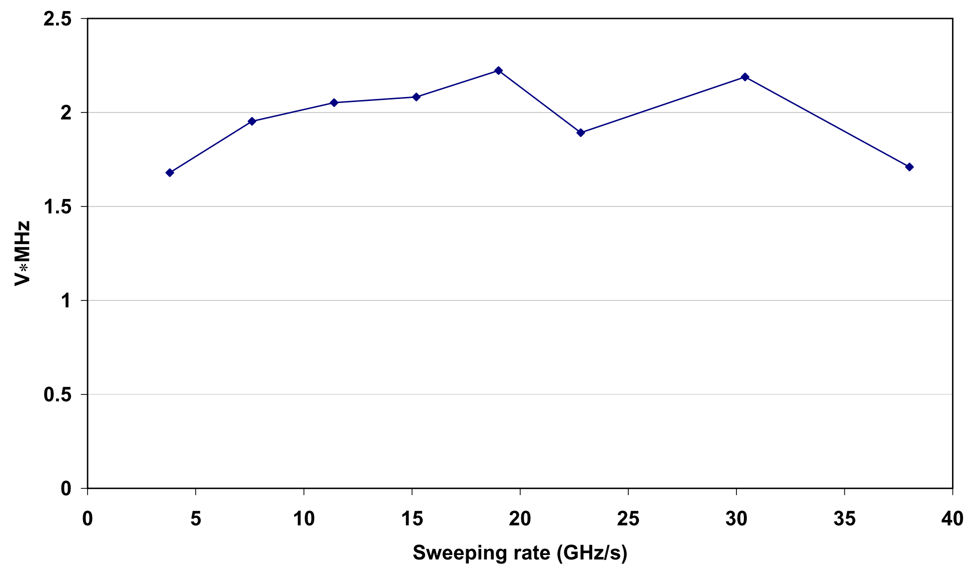


Fig. 6 The measured product $s\int_{-\infty}^{\infty}\langle I_t(t)\rangle\,\mathrm{d}t$ vs. s, the sweep rate of the cavity mode

different sweeping rates and the result is shown in Fig. 6. We can see that it is a constant, $\sim$2 V$\times$ MHz. With measured $T = 2.4$ ppm, detector quantum efficiency 0.95 A/W, detector gain 5×10^6 V/A, and incident power 2 mW, the quantity on the right of the above equation is about 1.7 V $\times$ MHz. This proves the validity of (23).

5 Conclusion

In this paper, we examined the dependence of the noise of the extracted decay rate in CW-CRDS on the extinction ratio of the light switch. We derived a simple analytical expression for the excess noise caused by a finite extinction ratio and experimentally tested our prediction by changing the residual RF power driving an AOM when it is turned off. The experimental results are in excellent agreement with the model. Our results show that for decay signals with initial signal-to-RMS-noise ratio of 1500, an extinction ratio of 75 dB is needed to reach the noise floor in decay rate fluctuations that are mainly due to detector noise and drifting. This required minimum extinction ratio is 10 dB higher than twice the signal-to-noise ratio expressed in dB that a simple argument predicts.

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Appendix

In this appendix we will derive some correlation functions useful for analyzing CW-CRDS experiments with excitation by a frequency-noisy laser. We consider the diode laser to have an output field given by

$$E_L(t) = E_{L0}\exp\bigl(-\mathrm{i}\omega t - \mathrm{i}\phi(t)\bigr), \tag{8}$$

with ϕ subject to a random walk such that the probability it will make a change $\Delta\phi$ in time Δt is given by [12, 14]

$$P(\Delta\phi,\Delta t) = \frac{1}{\sqrt{2\pi\sigma_\phi^2(\Delta t)}}\exp\left(-\frac{\Delta\phi^2}{2\sigma_\phi^2(\Delta t)}\right), \tag{9}$$

with $\sigma_\phi^2(\Delta t) = 2D|\Delta t|$ with D the diffusion constant for the phase. We can evaluate the correlation function of the laser field as

$$\begin{aligned}&\bigl\langle E_L^*(t)E_L(t+\Delta t)\bigr\rangle\\ &\quad= I_L\exp(-\mathrm{i}\omega\Delta t)\int P(\Delta\phi,\Delta t)\exp(-\mathrm{i}\Delta\phi)\,\mathrm{d}(\Delta\phi)\\ &\quad= I_L\exp(-\mathrm{i}\omega\Delta t)\exp\bigl(-D|\Delta t|\bigr),\end{aligned} \tag{10}$$

where $I_L = |E_{L0}|^2$ is the laser intensity. Note that D is the inverse of the laser field correlation time, $D = 1/\tau_L$. The spectral density of the laser is the Fourier transform of the field correlation function [14] and, given the exponential correlation function, this is Lorentzian which allows us to relate $D = \pi\Delta\nu_L$, where $\Delta\nu_L$ is the FWHM of the spectral density of the laser.

In order to evaluate intensity fluctuations, we need to evaluate the correlation function

$$\begin{aligned}&\bigl\langle E_L^*(t_1)E_L(t_2)E_L^*(t_3)E_L(t_4)\bigr\rangle\\ &\quad= I_L^2\exp\bigl(-\mathrm{i}\omega(t_{21}+t_{43})\bigr)\bigl\langle\exp\bigl(-\mathrm{i}(\phi_{21}+\phi_{43})\bigr)\bigr\rangle,\end{aligned} \tag{11}$$

where we have used the shorthand $\phi_{ij} = \phi(t_i) - \phi(t_j)$ and correspondingly for t_{ij}. For $t_1 < t_2 < t_3 < t_4$ (or the reverse),

$$\begin{aligned}&\bigl\langle\exp\bigl(-\mathrm{i}(\phi_{21}+\phi_{43})\bigr)\bigr\rangle\\ &\quad= \iiint\exp\bigl(-\mathrm{i}(\phi_{21}+\phi_{43})\bigr)P(\phi_{21},t_{21})P(\phi_{32},t_{32})\\ &\qquad\times P(\phi_{43},t_{43})\,\mathrm{d}(\phi_{21})\,\mathrm{d}(\phi_{32})\,\mathrm{d}(\phi_{43})\\ &\quad= \exp\bigl(-D(t_{21}+t_{43})\bigr).\end{aligned} \tag{12}$$

For $t_1 < t_3 < t_2 < t_4$, we use $\phi_{21}+\phi_{43} = \phi_{31}+2\phi_{23}+\phi_{42}$ to write

$$\begin{aligned}&\bigl\langle\exp\bigl(-\mathrm{i}(\phi_{21}+\phi_{43})\bigr)\bigr\rangle\\ &\quad= \iiint\exp\bigl(-\mathrm{i}(\phi_{21}+\phi_{43})\bigr)P(\phi_{31},t_{31})P(\phi_{23},t_{23})\\ &\qquad\times P(\phi_{42},t_{42})\,\mathrm{d}(\phi_{31})\,\mathrm{d}(\phi_{23})\,\mathrm{d}(\phi_{42})\\ &\quad= \exp\bigl(-D(t_{31}+2t_{23}+t_{42})\bigr)\\ &\quad= \exp\bigl(-D(t_{21}+t_{43})\bigr),\end{aligned} \tag{13}$$

which is the same form as (12). All 24 possible time-order permutations can be written as $\exp(-D(|t_{ab}|+|t_{cd}|))$ if t_a, t_c are the earlier and later times that E_L appears and t_b, t_d the earlier and later times that E_L^* appears. We now consider the light transmitted through the cavity, $E_t(t)$,

$$\begin{aligned}E_t(t) &= T\sum_n R^n E_L(t-nt_\mathrm{r})\\ &= TE_{L0}\mathrm{e}^{-\mathrm{i}\omega t}\sum_n\bigl(R\mathrm{e}^{\mathrm{i}\omega t_\mathrm{r}}\bigr)^n\mathrm{e}^{-\mathrm{i}\phi(t-nt_\mathrm{r})},\end{aligned} \tag{14}$$

where t_r is the cavity round trip time. On resonance, $\omega t_\mathrm{r} = 2\pi\times$ (an integer). Let $\delta\omega$ be the detuning from resonance. Assume that $1-R, \delta\omega t_\mathrm{r} \ll 1$ (i.e. we have a low-loss cavity and we are nearly resonant with a mode). In this limit, we can convert the sum into an integral:

$$\begin{aligned}E_t(t) &= \frac{T}{1-R}E_{L0}\mathrm{e}^{-\mathrm{i}\omega t}\frac{k}{2}\\ &\quad\times\int\exp\bigl(-kt'/2+\mathrm{i}\delta\omega t'-\mathrm{i}\phi(t-t')\bigr)\,\mathrm{d}t',\end{aligned} \tag{15}$$

where $k = (1-R^2)/t_\mathrm{r}$ is the cavity (power) decay rate. In this and the following integrals over time, we take the integral over $(0,\infty)$. From this, we can calculate the correlation function

$$\begin{aligned}&\bigl\langle E_t^*(t)E_t(t+\Delta t)\bigr\rangle\\ &\quad= \left(\frac{T}{1-R}\right)^2 I_L\mathrm{e}^{\mathrm{i}\omega\Delta t}\left(\frac{k}{2}\right)^2\\ &\qquad\times\iint\mathrm{e}^{-k(t_1+t_2)/2+\mathrm{i}\delta\omega(t_1-t_2)-D|t_2-t_1-\Delta t|}\,\mathrm{d}t_1\,\mathrm{d}t_2\\ &\quad= \left(\frac{T}{1-R}\right)^2 I_L\mathrm{e}^{\mathrm{i}\omega\Delta t}\left(\frac{kD\mathrm{e}^{-(k/2+\mathrm{i}\delta\omega)\Delta t}}{2(D^2-(\frac{k}{2}+\mathrm{i}\delta\omega)^2)}\right.\\ &\qquad\left.-\frac{k^2\mathrm{e}^{-D\Delta t}}{4((D-\mathrm{i}\delta\omega)^2-(k/2)^2)}\right).\end{aligned} \tag{16}$$

In most cases relevant to CRDS, $D \gg k$, so the first term in the last bracket dominates and thus the correlation time of the transmitted field is $2/k = 2\tau$, i.e. twice the cavity decay rate. With $\Delta t = 0$, we have the mean transmission

$$\begin{aligned}\bigl\langle I_t(t)\bigr\rangle &= \left(\frac{T}{1-R}\right)^2 I_L\left(\frac{(D+k/2)(k/2)}{(D+k/2)^2+\delta\omega^2}\right)\\ &\xrightarrow{\delta\omega=0}\left(\frac{T}{1-R}\right)^2 I_L\left(\frac{1}{1+2\pi\tau\Delta\nu_L}\right),\end{aligned} \tag{17}$$

where we have used $D = \pi \Delta\nu_L$ and $k = 1/\tau$. This last equation can be more directly derived from the convolution of the Lorentzian spectral density of the input laser with the Lorentzian transmission profile of the optical cavity.

We now consider intensity fluctuations. When the cavity is under steady-state excitation by a laser with spectral phase diffusion, the interference of light that enters the cavity at different times will cause intensity noise: $\langle \delta I_t(t)\delta I_t(t + \Delta t)\rangle = \langle I_t(t)I_t(t + \Delta t)\rangle - \langle I_t(t)\rangle^2$. We can express the mean second order intensity as

$$\begin{aligned}
&\langle I_t(t)I_t(t+\Delta t)\rangle \\
&= \langle E_t^*(t)E_t(t)E_t^*(t+\Delta t)E_t(t+\Delta t)\rangle \\
&= \left(\frac{T}{1-R}\right)^4 I_L^2 \left(\frac{k}{2}\right)^4 \\
&\quad \times \iiiint e^{-(k/2)(t_1+t_2+t_3+t_4)+i\delta\omega(t_1-t_2+t_3-t_4)} \\
&\quad \times \langle \exp\big(\phi(t-t_1) - \phi(t-t_2) + \phi(t+\Delta t - t_3) \\
&\quad - \phi(t+\Delta t - t_4)\big)\rangle \, dt_1\, dt_2\, dt_3\, dt_4 \\
&= \left(\frac{T}{1-R}\right)^4 I_L^2 \left(\frac{k}{2}\right)^4 e^{-k(2t+\Delta t)} \\
&\quad \times \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t} dt_2 \int_{-\infty}^{t+\Delta t} dt_3 \int_{-\infty}^{t+\Delta t} e^{-k(t_1+t_2+t_3+t_4)} \\
&\quad \times \big\{4\big(1 + 2H(t-t_3) + H(t-t_4)\big)e^{D(t_1-t_2+t_3-t_4)} \\
&\quad \times \cos\big(\delta\omega(t_1-t_2)\big)\cos\big(\delta\omega(t_3-t_4)\big) \\
&\quad + 2H(t-t_3)\big(1+H(t-t_4)\big)e^{D(t_1+t_2-t_3-t_4)} \\
&\quad \times \cos\big(\delta\omega(t_1+t_2-t_3-t_4)\big)\big\},
\end{aligned} \tag{18}$$

where we have again made the assumptions that $1 - R \ll 1$ and that we are close to resonance with a cavity mode with detuning $\delta\omega$, so that we can replace the sums over passes by integrals over time inside the cavity. We have also used the Heaviside step function $H(x) = 1$ for $x > 0$ and $= 0$ for $x < 0$. In general, evaluation of this four-dimensional integral will produce a complicated analytical result. However, we note that the average over the phase random walk will give a nearly zero result unless one of two pairs of conditions holds: (1) $t_1 \sim t_2$ and $t_3 \sim t_4$ or (2) $t_4 \sim t_1 + \Delta t$ and $t_3 \sim t_2 + \Delta t$, where by $\sim$ is meant that the absolute value of the difference is on the order of $1/D$. For $D \gg k$, there is negligible contribution from those narrow regions where both sets of conditions hold simultaneously (where we would have contributions from such as (13)). When the regions are distinct, the phase average can be evaluated by (12). Using this over the full domain, each condition gives a factor of two integrals that are essentially the same as the integral in (16), and we find that

$$\langle I_t(t)I_t(t+\Delta t)\rangle \xrightarrow{D\gg k} \langle I_t(t)\rangle^2\big(1 + e^{-k\Delta t}\big). \tag{19}$$

This shows that, in this limit, the intensity fluctuations decay with the cavity power decay rate, k, and that $\sigma^2(I_t(t)) = \langle I_t(t)\rangle^2$, which is consistent with the χ^2 with two degrees of freedom prediction for the intensity distribution as predicted earlier using the central limit theorem. We note that this result does not depend on the relative values of D and $\delta\omega$.

If we restrict our attention to $\Delta t = 0$, then the integrals in (18) can be considerably simplified. This leads to the following expression for the variance of the intensity:

$$\begin{aligned}
&\langle I_t(t)^2\rangle - \langle I_t(t)\rangle^2 \\
&= \langle I_t(t)\rangle^2 \left[\frac{(2D)(2D+3k)[(2D+k)^2 + 4\delta\omega^2]}{(2D+k)^2[(2D+3k)^2+4\delta\omega^2]}\right] \\
&\xrightarrow{D\gg k} \langle I_t(t)\rangle^2,
\end{aligned} \tag{20}$$

in agreement with the argument above.

We now consider the case where the input laser is subjected to a linear frequency sweep though a cavity resonance. This is equivalent to the case where the laser is fixed in frequency but the cavity resonances are shifted through resonance. In this case, we have for the laser field

$$E_L(t) = E_{L0}\exp\big(-i(\omega_0 t + \pi s t^2 + \phi(t))\big), \tag{21}$$

where s is the frequency sweep rate (Hz/s) and $\phi(t)$ is assumed to undergo the same phase diffusion. This equation gives an instantaneous laser angular frequency of $\omega(t) = \omega_0 + 2\pi s t$. For convenience, we take $t = 0$ to be the time that the laser goes through resonance with the cavity, i.e. $\omega_0 t_r = 2\pi \times$ (an integer). Again, taking limits such that we can convert the sum over passes to an integral, we obtain for the field transmitted by the cavity

$$\begin{aligned}
E_t(t) &= \left(\frac{T}{1-R}\right) E_{L0}\left(\frac{k}{2}\right)\exp(-i\omega_0 t) \\
&\quad \times \int \exp\left(-\frac{k}{2}t_1 - i\pi s(t-t_1)^2 + \phi(t-t_1)\right) dt_1.
\end{aligned} \tag{22}$$

We can now evaluate the average intensity as a function of time:

$$\begin{aligned}
\langle I_t(t)\rangle &= \left(\frac{T}{1-R}\right)^2 I_L \left(\frac{k}{2}\right)^2 \\
&\quad \times \iint \exp\big(-(k/2)(t_1+t_2) \\
&\quad + i\pi s\big((t-t_1)^2 - (t-t_2)^2\big) - D|t_1 - t_2|\big)\, dt_1\, dt_2,
\end{aligned} \tag{23}$$

where, as above, the $-D|t_1 - t_2|$ term arises from the stochastic phase diffusion of the input laser.

This expression, without the phase-diffusion term, has appeared in numerous prior papers, including [15, 16]. For $D = 0$, the two integrals factor (one being the complex conjugate of the other); each integral can be expressed as a complementary error function with a complex argument:

$$\langle I_t(t)\rangle \overset{D->0}{\longrightarrow} \left(\frac{T}{1-R}\right)^2 I_L\left(\frac{k^2}{16s}\right)\mathrm{e}^{-kt}\left|\mathrm{erfc}\left(\frac{k+4\pi \mathrm{i} st}{4\sqrt{-\mathrm{i}\pi s}}\right)\right|^2$$
$$\approx \left(\frac{T}{1-R}\right)^2 I_L\left(\frac{k^2}{4s}\right)\mathrm{e}^{-kt}, \qquad (24)$$

where $\approx$ refers to estimation of the integral by the stationary phase approximation. The stationary point is $t_1 = t$ and applies when $t \gg 1/\sqrt{|s|}$, which is the width of the time interval that dominates the integral, i.e. the effective time that light is injected into the cavity. This approximation misses the rapid beating in the exact solution, which is due to the sharp cut off of the integral at $t_1 = 0$ instead of $-\infty$.

This case of exciting a cavity by a frequency-noisy swept laser was previously treated by Morville et al. [12]; they presented Monte Carlo simulations of phase diffusion to calculate the transmission and averaged different runs to calculate $\langle I_t(t)\rangle$. Here, we exploit the analytical expression for the field correlation function, represented by (23), to provide analytical expressions for the mean transmission in this case. With a finite laser frequency noise ($D > 0$), the double integral in (23) no longer factors. If we change integration variables to $x = t_1 - t_2$ and $y = (t_1 + t_2)/2$ (within domains $(-2y, +2y)$ and $(0, \infty)$, respectively), we can explicitly perform the integration over x to give

$$\langle I_t(t)\rangle = \left(\frac{T}{1-R}\right)^2 I_L\left(\frac{k^2}{2D}\right)\mathrm{e}^{-kt}\int_0^\infty \frac{\mathrm{e}^{-ky}}{1+(\frac{2\pi s(y-t)}{D})^2}$$
$$\times\left(1-\mathrm{e}^{-2Dy}\left(\cos\big(4\pi s(y-t)y\big)\right.\right.$$
$$\left.\left.-\frac{2\pi s(y-t)}{D}\sin\big(4\pi s(y-t)y\big)\right)\right)\mathrm{d}y. \qquad (25)$$

For $D \gg k, \sqrt{2\pi s}$, $\exp(-2Dy) \ll 1$ for most of the important part of the integration domain of y and we can neglect these terms. In terms of a dimensionless sweep rate, $\beta = 2\pi s/(kD)$, we can write the average transmission as a function of time relative to passing through resonance as

$$\langle I_t(t)\rangle \overset{D\gg k,\sqrt{2\pi s}}{\longrightarrow} \left(\frac{T}{1-R}\right)^2 I_L\left(\frac{k}{2D}\right)\mathrm{e}^{-kt}$$
$$\times\int_{-\infty}^{kt}\frac{\mathrm{e}^u}{1+(\beta u)^2}\,\mathrm{d}u. \qquad (26)$$

The factor in front of $\exp(-kt)$ is the mean transmission if the laser was centered on the cavity resonance. The integral can be evaluated in terms of the imaginary part of the exponential $n = 1$ integral with complex argument,

$$\int_{-\infty}^{kt}\frac{\mathrm{e}^u}{1+(\beta u)^2}\,\mathrm{d}u$$
$$= \beta^{-1}\Im\big(E_1\big(-\mathrm{i}\beta^{-1} - kt\big)\exp\big(-\mathrm{i}\beta^{-1}\big)\big). \qquad (27)$$

Alternatively, the integral can be evaluated numerically as the integrand is monotonic. Values needed for the calculation of $\langle I_t(t)\rangle$ over the full range of time are calculated by a single sum over time intervals. Note that in this limit that the transmission is reduced by a factor that depends only on the reduced frequency sweep rate, β, and the reduced time, kt. The reduced time corresponding to the peak of $\langle I_t(t)\rangle$ is 1 for $\beta \ll 1$, and approaches zero for $\beta \gg 1$, with a value of 0.5 for $\beta = 1.4$. The peak cavity transmission is smaller than that of the unswept laser by a factor that approaches unity as $\beta \to 0$, is 0.5 for $\beta = 2.4$, and slowly $\to \pi/\beta$ for $\beta \gg 1$.

It is worth noting that, for finite D, $\langle I_t(t)\rangle$ is proportional to t^{-2} for large t, not $\exp(-kt)$ as for excitation by a monochromatic laser. There have been several previous reports [16–18] of using the transient response of a cavity excited by a frequency-swept laser to determine the cavity loss rate, k. These have assumed that $\langle I_t(t)\rangle$ is proportional to $\exp(-kt)$, which the present analysis demonstrates is not rigorously correct.

The intensity correlation function, $\langle I_t(t)I_t(t+\Delta t)\rangle$, reduces to evaluation of the same integral form as (18), but with $\pi s t_i^2$ replacing each $\delta\omega t_i$ term. In general, these integrals do not have simple closed-form expressions and numerical evaluation is challenging due to the highly oscillatory integrands. The calculation of $\langle I_t(t)^2\rangle$ will reduce to, for $D \gg k, \sqrt{2\pi s}$, a pair of products of two integrals that are each $\langle I_t(t)\rangle$ (as above for the unswept case), so we again have χ^2 with two degrees of freedom fluctuations. This can be rationalized because, in the frequency-swept case, the cavity is excited for an effective time of $\sim 1/\sqrt{2\pi s}$ and if this is many coherence times of the laser, $1/D$, we expect the central limit theorem result to apply. For the very rapid sweep case, $2\pi s \gg D^2$, then (25) is dominated by the last term and we obtain a result that is independent of D, as we would expect since in this limit we are exciting the cavity for an effective time that is short compared to the dephasing time of the laser. Note that, for $D \sim 10^7\ \mathrm{s}^{-1}$, as appropriate for single mode diode lasers, $2\pi s = D^2$ at a sweep rate of 1.6 THz/s, more than two orders of magnitude higher than we use in our experiments. For external cavity diode lasers, however, $D \sim 10^5\ \mathrm{s}^{-1}$ applies, so that the experimental sweep rate would put one in this very rapid sweep limit where the phase noise of the laser is irrelevant and one would have reproducible excitation of the cavity.

References

1. A. O'Keefe, D.A.G. Deacon, Rev. Sci. Instrum. **59**, 2544 (1988)
2. R.T. Jongma, M.G.H. Boogaarts, I. Holleman, G. Meijer, Rev. Sci. Instrum. **66**, 2821 (1995)
3. J.B. Dudek, P.B. Tarsa, A. Velasquez, M. Wladyslawski, P. Rabinowitz, K.K. Lehmann, Anal. Chem. **75**, 4599 (2003)
4. M.J. Thorpe, K.D. Moll, R.J. Jones, B. Safdi, J. Ye, Science **311**, 1595 (2006)
5. D. Romanini, K.K. Lehmann, J. Chem. Phys. **99**, 6287 (1993)
6. K.K. Lehmann, U.S. Patent 5,528,040, 1996
7. D. Romanini, A.A. Kachanov, N. Sadeghi, F. Stoeckel, Chem. Phys. Lett. **264**, 316 (1997)
8. K.K. Lehmann, H. Huang, Optimal signal processing in cavity ring-down spectroscopy, in *Frontiers of Molecular Spectroscopy*, ed. by J. Laane (Elsevier, Amsterdam, 2008), pp. 632–658
9. H. Huang, K.K. Lehmann, Opt. Express **15**, 8745 (2007)
10. K.W. Busch, M.A. Buscheds, *Cavity Ringdown Spectroscopy: An Ultratrace-Absorption Measurement Technique*. ACS Symp. Ser., vol. 720 (Oxford University Press, Washington, 1999)
11. K. Petermann, *Laser Diode Modulation and Noise* (Kluwer Academic, Tokyo, 1988)
12. J. Morville, D. Romanini, M. Chenevier, A.A. Kachanov, Appl. Opt. **41**, 6980 (2002)
13. T. Okoshi, K. Kikuchi, Nakayama, Electron. Lett. **16**, 630 (1980)
14. C.H. Henry, IEEE J. Quantum Electron. **QE-18**, 259 (1982)
15. Z. Li, G.E. Stedman, H.R. Bilger, Opt. Commun. **100**, 240 (1993)
16. J. Poirson, F. Bretenaker, M. Vellet, A.L. Floch, J. Opt. Soc. Am. B **14**, 2811 (1997)
17. Y.B. He, B.J. Orr, Chem. Phys. Lett. **319**, 131 (2000)
18. Y.B. He, B.J. Orr, Chem. Phys. Lett. **335**, 215 (2001)