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Cavity ring-down spectroscopy with Fourier-transform-limited light pulses

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Abstract

We have investigated the implications of using a pulsed, nearly Fourier-transform-limited, single-mode light source for cavity ring-down spectroscopy (CRDS) in the mid-infrared spectral range. We show that in the case where the coherence time and duration of the light pulse exceeds the cavity roundtrip time, mode beating generates oscillations in the ring-down waveform. When the period of the oscillations is comparable to the ring-down time, it becomes difficult to obtain meaningful decay constants. This situation can be avoided by careful choice of cavity geometry and mode matching conditions together with suitable electronic filtering.

1. Introduction

Cavity ring-down spectroscopy (CRDS) is an ultrasensitive absorbance measurement technique owing to its insensitivity to intensity fluctuations of pulsed light sources and the multipass nature of the probe light interaction with the absorber of interest. In the visible and UV regions, CRDS has been successfully applied to a variety of systems: absorption spectroscopy of jet-cooled metal clusters and small molecules [1], determination of optical gain in a chemically pumped BiF laser system [2], kinetic studies of phenyl radical reactions [3,4], measurement of OH concentrations and temperature in flames [5], overtone spectroscopy of HCN isotopomers [6,7], determination of absolute transition strengths in CO molecules [8] and quantitative diagnostics of CH_3 concentration in a hot-filament reactor for diamond chemical vapor deposition (CVD) [9,10].

Recently, Scherer et al. [11] extended CRDS into the infrared using an optical parametric oscillator (OPO). This wavelength region is of particular significance because many molecular species have characteristic spectra in the 1–10 μm range. In their studies Scherer et al. used a nearly Fourier-transform-limited pulse and observed no significant changes in the cavity transmission coefficient when they scanned the laser frequency over a range corresponding to a couple of longitudinal mode spacings. It was assumed that only longitudinal modes were excited and the laser bandwidth was smaller than the

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cavity mode spacing. This interpretation is surprising in light of previous work by Meijer et al. [5] which indicated modulation in the cavity output signal for similar cavity geometries and corresponding mode structures. The results of Ref. [11] were also interpreted to contradict the predictions of Zalicki and Zare [12], who claimed that frequency selectivity in a ring-down cavity could bias measurements. Because of this apparent difference in interpretation, several groups [13,14] have been independently motivated to re-examine the response of a Fabry–Perot cavity to a Fourier-transform-limited pulse incident upon it.

We have performed experiments using the same type of OPO as Ref. [11] in which we examined the ring-down waveform from symmetric and half-symmetric resonators having a length of approximately half a meter. We find pronounced mode-beating effects that can completely alter the overall ring-down waveform. We have also developed a theoretical description for the response of a Fabry–Perot resonator to incident pulses of Fourier-transform-limited light. This treatment is based on the well-known semiclassical cavity differential equations described by Siegman [15]. Although our treatment differs from that of Hodges et al. [13], our results are in direct qualitative agreement with them.

2. Coherent light pulses in Fabry–Perot cavities

Most of the previously performed CRDS experiments involved pulses having much larger spectral bandwidths than predicted by the Fourier-transform limit of their time-domain waveforms, which indicate that the phase of the electric field forming the pulse undergoes fluctuations. These fluctuations wash out coherent superposition effects of the pulse in the cavity. In contrast, pulses generated by an OPO system are almost transform-limited, so that for example a pulse of a 4 ns FWHM has a coherence time [4] slightly shorter than 4 ns, and a bandwidth that is only slightly larger than the corresponding 110 MHz bandwidth in the Fourier limit at FWHM.

[4] The coherence time is given by the width of the first-order correlation function $G^{(1)}(\tau) = \langle E(t)E(t+\tau)\rangle / \langle E^2(t)\rangle$, where $E(t)$ is the pulse amplitude at time t. In this definition the coherence time is limited by both the pulse envelope and phase fluctuations.

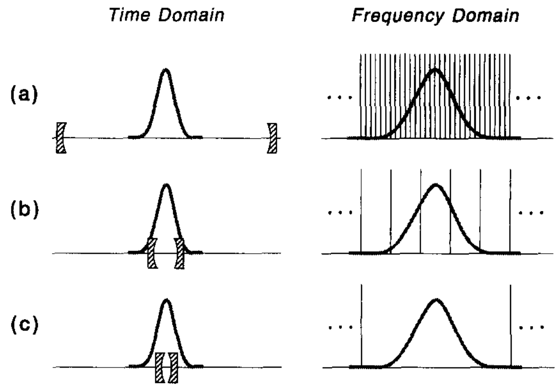

Fig. 1. Illustration of the interaction of an empty Fabry–Perot cavity with a Fourier-transform-limited Gaussian light pulse in the time and frequency domains: (a) the pulse duration is much shorter than the cavity roundtrip time; (b) the pulse duration and the cavity roundtrip time are comparable; and (c) the pulse duration is much longer than the cavity roundtrip time.

In the following section we discuss the behavior that arises for Fourier-transform-limited light pulses. We distinguish three different experimental situations (Fig. 1) based on a fixed pulse duration and a variable cavity roundtrip time:

1. The pulse duration is much shorter than the cavity roundtrip time.
2. The pulse duration and the cavity roundtrip time are comparable.
3. The pulse duration exceeds the cavity roundtrip time.

The first situation probably represents the most intuitive picture of CRDS. The pulse can be viewed as a particle bouncing between two mirrors in which a small part of the pulse is transmitted each time the pulse hits a mirror surface (Fig. 1a). The cavity output then consists of a train of pulses with exponentially decreasing maxima. The pulse never overlaps inside the cavity, and consequently interference phenomena cannot occur. In the frequency domain, we find that the free spectral range (FSR) of the cavity is much smaller than the pulse bandwidth for this situation so that the cavity transmits the pulse on many cavity modes. The cavity output appears as pulses in time, which in frequency space, corresponds to the superposition of many cavity modes. As will be shown in Ref. [13], mode beating can be observed also in this situation.

In the second case (Fig. 1b), the pulse duration approximately equals the roundtrip time in the cavity. In the frequency domain, this condition implies that the laser spectrum overlaps only a few cavity modes. In the third case (Fig. 1c), the pulse duration is much longer than the roundtrip time. This condition results in a cavity FSR exceeding the laser bandwidth. If the center frequency of the pulse lies between two cavity modes, almost no light will be transmitted by the cavity. This situation makes it impossible to scan the laser frequency and record continuous absorption spectra. In the time domain, a short cavity can be seen as producing significant pulse overlap. Owing to the coherence of the pulse, this overlap leads to interference of the light inside the cavity. Consequently, for some conditions the intensity of the output of the cavity may fall below the detection threshold.

By its very definition, high-resolution laser spectroscopy requires narrow linewidth light sources. For example, the laser linewidth should be limited to at most a few hundred MHz to resolve fully typical vibration–rotation transitions of gaseous molecules. In the case of Fourier-transform-limited laser pulses, this small bandwidth corresponds to a pulse duration in the nanosecond range. Moreover, simple cavity alignment and easy handling dictate in general that a practical ring-down cavity should not exceed 1 to 2 m in length. In most cases the pulse duration is slightly larger than the cavity roundtrip time (Fig. 1b), leading to pulse self-overlap within the cavity with a laser linewidth extending over several, but not many, cavity modes. For example, in a confocal resonator of 0.5 m in length, the minimum mode spacing is $c/(4L) = 150$ MHz, so that a typical laser power spectrum density width of 110 MHz at FWHM (4 ns pulse intensity width at FWHM) overlaps at least 2 cavity modes. Conditions of zero pulse overlap are difficult to achieve because of the limitations set by both the laser spectral resolution and the length of the ring-down cavity. Consequently, interference effects in CRDS are common and cannot be ignored in general.

In what follows, we briefly describe our experimental setup, present experimental results, introduce a time domain model of cavity dynamics, and compare theoretical predictions based on this model to our experimental data.

3. Experimental

A Nd:YAG laser-pumped OPO system (Continuum Mirage 3000) is used to generate nearly Fourier-transform-limited Gaussian light pulses, approximately 4 ns in length, at a repetition rate of 10 Hz. An upper bandwidth limit of 500 MHz (0.017 cm^{-1}) was specified by the manufacturer. The wavelength can be tuned from 1.5 to 4.0 μm, with maximum pulse energies of 8 mJ, decreasing to about 1 mJ at the edges of the tuning range.

Fig. 2 presents a schematic overview of the experimental setup. The pulse generated by the OPO system travels a distance of 1.5 m and enters an optical cavity, consisting of two mirrors. In one configuration (not shown in Fig. 2), we use a 52 cm long half-symmetric resonator consisting of one plane mirror and one curved mirror or 1 m radius both having a reflectivity greater than 99% at 3.17 μm. In another configuration (shown in Fig. 2) we use a 41 cm long symmetric resonator consisting of two mirrors with 2 m radii both having a reflectivity greater than 99% at 3.17 μm. The mirrors were coated by Rocky Mountain Instruments, Longmont, CO. The two mirrors are mounted as windows on the cell flanges, thereby sealing the ends of the vacuum cell against atmospheric pressure. Flexible bellows allow adjustment of the mirrors with micrometer screws. For the data presented, the cell is evacuated with a rotary pump to a residual pressure of 20×10^{-3} Torr. The cavity output radiation is incident on a

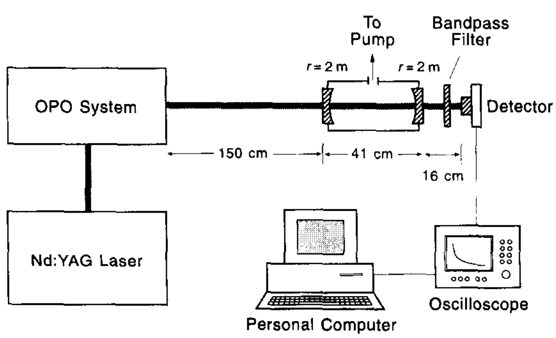

Fig. 2. Schematic view of the experimental setup.

bandpass interference filter centered at 3.2 μm and with 0.15 μm FWHM transmission band (Janos Technology, Townshend, VT). Upon exiting the optical cavity, the radiation is detected with a liquid nitrogen-cooled HgCdTe IR detector (Model 90-5131, Hughes, Electronics, Goleta, CA). The diode is directly connected to an amplifier with 600 MHz (−3 dB attenuation) bandwidth. A digital oscilloscope (HP 54510A) records the ring-down waveforms at a 1 GSa/s sampling rate and stores up to 296 single-shot traces in real time. After the scope memory is filled, all traces are transferred to a personal computer, where they are summed and an average waveform is calculated.

4. Results

Fig. 3 presents ring-down profiles for the two optical cavity configurations obtained by averaging

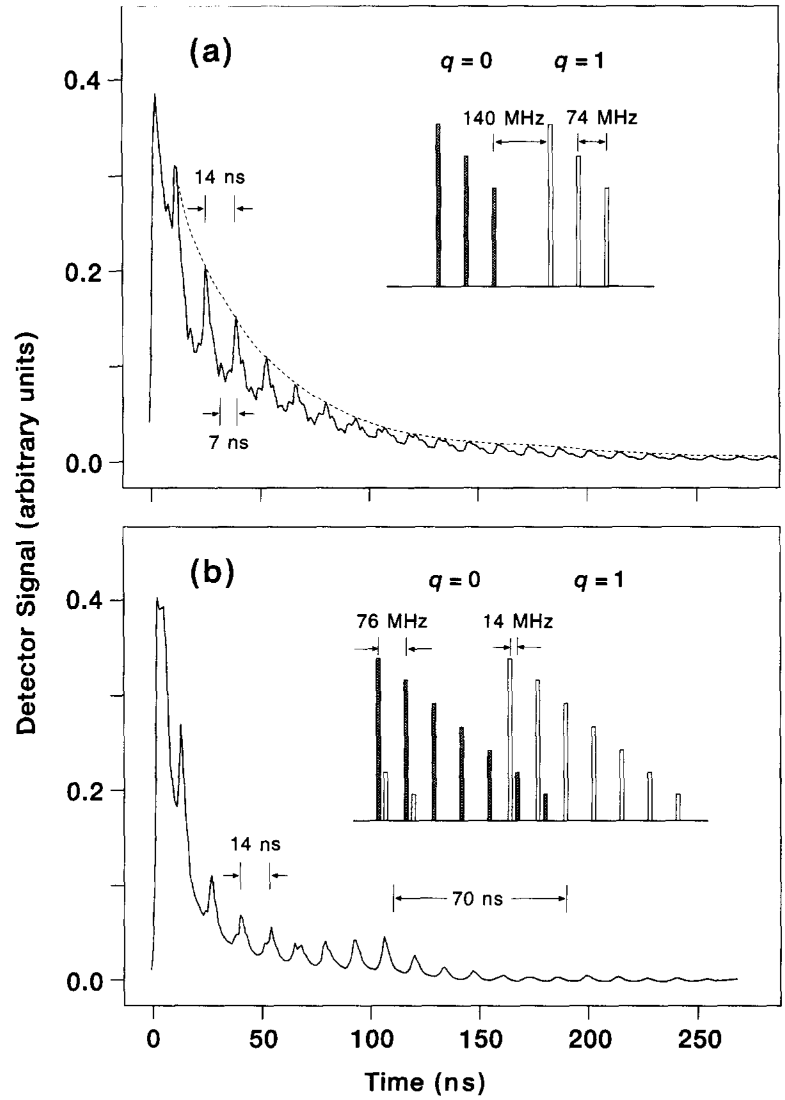

Fig. 3. Experimentally observed cavity decay waveform: (a) for a half symmetric cavity configuration of 52 cm length, with a plane mirror and a mirror of 1 m curvature; and (b) for a symmetric cavity configuration of 41 cm length with 2 m curvature mirrors. The traces are summed and averaged for 296 single shot waveforms.

296 single shots. The ring-down waveform for the half-symmetric resonator (Fig. 3a) shows exponential decay upon which is superimposed a rapid modulation in which the peaks are separated by 14 ns. Note that the observation of these beats is made possible by our use of a fast detector; if a slow detector had been used instead, the beats would have been averaged out and the waveform would have appeared to be a simple exponential [5].

Fig. 3b presents ring-down waveforms for the symmetric optical resonator from which two different beat periods are seen. The clearly visible fast oscillations are separated again by 14 ns, whereas a less pronounced second beat period of approximately 70 ns is also apparent. Once again, this information is the consequence of using a fast-response detector; if a slow detector had been used instead, the rapid modulation would have been averaged out, but non-exponential behavior caused by the slower beat period would remain nevertheless.

5. Discussion

Mode-beating effects are clearly demonstrated in the data presented in Fig. 3 for a Fourier-transform-limited pulse incident on an optical cavity of practical dimensions, either a 52 cm long half-symmetric resonator (Fig. 3a) or a 41 cm long symmetric resonator (Fig. 3b) [6]. To understand the origin of this behavior we consider the mode structure of these two fixed resonator geometries. Then we compare our measurements to the results derived from a semiclassical treatment of Fabry–Perot resonator dynamics.

[5] Indeed, a slower detector was used in Ref. [11]. This explains why fast beat oscillations were not observed. In addition, Ref. [11] neglected the existence of transverse modes in the optical cavity. A more detailed discussion of why Ref. [11] failed to detect mode-beating effects is presented in Ref. [13].

[6] The modulation we observed should be distinguished from that reported by K. An, et al. [16], who used a cw excitation source and swept the length of the optical resonator. The origin of this latter modulation is the interference between the probe laser and the intracavity field.

5.1. Cavity mode structure

In general, a Fabry–Perot resonator has both longitudinal and transverse eigenfrequencies. The frequency of a mode having longitudinal index q and transverse indices m,n (TEM_{mn} mode), is given by (see e.g. Ref. [15] Ch. 19):

$$\nu_{qmn} = \frac{\omega_{qmn}}{2\pi} = \frac{c}{2L}\left[q + (n+m+1)\frac{\cos^{-1}\left(\pm\sqrt{g_1 g_2}\right)}{\pi}\right], \quad (1)$$

where the two different mirrors have radii r_1 and r_2, separation L, and $g_1 = 1 - L/r_1$ and $g_2 = 1 - L/r_2$. The specific cases of symmetric and half-symmetric cavity modes can easily be derived from this equation.

We assume that for the half-symmetric cavity only longitudinal and transverse TEM_{mn} modes with indices $m \in \{0, \ldots, 2\}$ and $n = 0$ are excited. The inset in Fig. 3a shows the mode frequencies. The smaller mode spacing of 74 MHz results in oscillations with a 14 ns repetition period, while a second interval, nearly twice as large, results in additional oscillations with a 7 ns period. Although the waveform is modulated by two different beat frequencies, the ring-down profile retains its exponential decay profile because both frequencies are large and can be eliminated using a low pass filter.

The inset in Fig. 3b shows the mode frequency positions in the symmetric cavity, assuming that longitudinal and transverse TEM_{mn} modes with indices ranging from $m \in \{0, \ldots, 4\}$ and $n \in \{0, \ldots, 3\}$ are excited. Once again the fast oscillations are characterized by a 14 ns period, close to the theoretically expected value of 13 ns, caused by a longitudinal mode spacing of 76 MHz. Additional frequencies with a decay period of 70 ns are present, however, arising from higher order transverse modes and having a spacing of 14 MHz. Thus, the ring-down waveform is modulated by two different beat frequencies.

For slow modulation conditions, the problem arises of extracting the ring-down decay time constant from the waveform, because it is relatively straightforward to average out the high-frequency beating modes with a low pass filter, but it is obviously difficult to eliminate the slow amplitude modulation caused by transverse mode beating. It is therefore very important to design and mode-match cavities in order to avoid such closely spaced transverse mode patterns.

5.2. Semiclassical cavity rate equations

We have performed extensive theoretical modeling to confirm our results and to gain more insight into passive resonator dynamics. Our calculations are based on laser cavity differential equations for the electric field, the polarization, and the population density of the medium inside the cavity. These equations are derived and explained in detail in Ref. [15]. In the following we briefly summarize the theoretical treatment necessary to describe the observed effects in an empty cavity.

Considering classical light fields, the derivation of the cavity differential equations starts with Maxwell's equations, describing the evolution of the electric field in time and space, $\mathscr{E}(r,t)$. The fields inside a Fabry–Perot cavity can be decomposed using the normal mode expansion, such that each cavity mode, $u_n(r)$, representing the field spatial distribution, is multiplied by a coefficient, $\hat{E}_n(t)$, representing the time-dependent part:

$$\mathscr{E}(r,t) = \sum_n \hat{E}_n(t) u_n(r). \tag{2}$$

Applying the 'slowly varying envelope approximation' to the time-dependent part:

$$\hat{E}_n(t) = \tfrac{1}{2}\left(E_n(t)e^{i\omega t} + \text{c.c.}\right), \tag{3}$$

leads to the so-called 'neoclassical equations of laser theory' (Ref. [15], p. 943) for the envelope $E_n(t)$ of the electric field, and generally also for the polarization $P_n(t)$ and inversion $\Delta N(t)$ of the medium. For the trivial case of an empty cavity the polarization and the inversion are always zero. Results including the presence of an absorber inside the optical cavity and a full numerical treatment for CRDS, will be presented elsewhere [17].

Because we consider an empty cavity here, only one equation for the electric field amplitude remains:

$$\frac{dE_n(t)}{dt} + \left[\gamma_c/2 + i(\omega - \omega_n)\right]E_n(t) = \left(\frac{2\gamma_e}{\varepsilon V_c}\right)^{1/2} E_e(t), \tag{4}$$

where ω represents the frequency of the external field $\mathscr{E}_c(t)$, and ε is the dielectric constant. The total cavity losses γ_c, comprise internal losses $\gamma_0 = 2\alpha_0 c$, and coupling losses γ_e. For a roundtrip transit time T, with mirror power reflectivities R, we get:

$$\gamma_c = \gamma_0 + \gamma_e = 2\alpha_0 c + \frac{1}{T}\ln(1/R), \tag{5}$$

where α_0 is the scattering loss coefficient. The amplitude of the external field contains the somewhat arbitrary normalization constant V_c, of the cavity mode volume.

A numerical treatment can be used to explain the occurrence of beat oscillations as a dominant feature in ring-down behavior. By integrating Eq. (4) for parameters describing our experimental conditions (see the figure caption for explicit values), we are able to show that the long and short oscillation periods of the mode beating are a function of cavity geometry.

Given the normal mode expansion (see Eq. (2)) of the fields inside the cavity, the spatial solutions of Maxwell's equations (i.e. the cavity geometry) directly determine the eigenfrequencies, ω_n. Therefore, if the bandwidth of the laser pulse overlaps with a set of frequencies, ω_n, $n \in \{1, \ldots, N\}$, it becomes necessary to solve the corresponding set of N coupled differential equations given by Eq. (4), where each equation set accounts for one excited mode eigenfrequency within the spectral range of the pulse.

Consequently, each solution has a different phase arising from the different detunings $(\omega - \omega_n)$ of the laser frequency with respect to the cavity modes. The intensity at the detector position is then given by the squared magnitude of the sum of the electric field components of all the excited modes in the cavity:

$$I(t) \propto \left|\sum_{n=1}^{N} E_n(t)\right|^2. \tag{6}$$

This summation of modes leads to mode beating in the ring-down waveform.

5.3. Comparison with measurements

Numerical solutions of Eq. (4) are given in Fig. 4 for two different model spectra. If a spectral comb of modes separated by 76 MHz is considered, purely exponential decay modulated only by the corresponding fast beat period is observed (dotted line). If it is assumed that two such combs exist and are shifted by 14 MHz from one another, an additional modulation with a slow period of 70 ns appears in the decay (solid line). The high modulation index observed in the theoretical mode beating curves is a consequence of the assumptions that the input pulse is truly Fourier-transform-limited and that all cavity modes are equally weighted. Clearly, this simple spectral model verifies (compare Figs. 3 and 4) that the excitation of closely spaced modes causes the appearance of mode beating in the output from the passive optical resonator and changes the exponential decay waveform substantially.

5.4. Concluding remarks

We have investigated the response of Fabry–Perot resonators to a single-mode, Fourier-transform-limited light pulse. We find that when the bandwidth of such a coherent pulse overlaps two or more cavity modes, the output signal will be amplitude modulated, arising from mode beating. The beat period is determined by the frequency separation of the excited cavity modes. Depending on cavity geometry, the existence and excitation of higher order transverse cavity modes can lead to fast and slow beat periods.

Observation of mode-beating effects in the ring-down waveform indicates that the coherence time of the light source under investigation exceeds the cavity roundtrip time. Consequently, a simple exponential decay of the waveform is not expected in general and failure to recognize the importance of interference effects can significantly bias the interpretation of ring-down spectra. Conversely, by paying careful attention to mode matching of the light source to the cavity, it is possible to achieve simple exponential

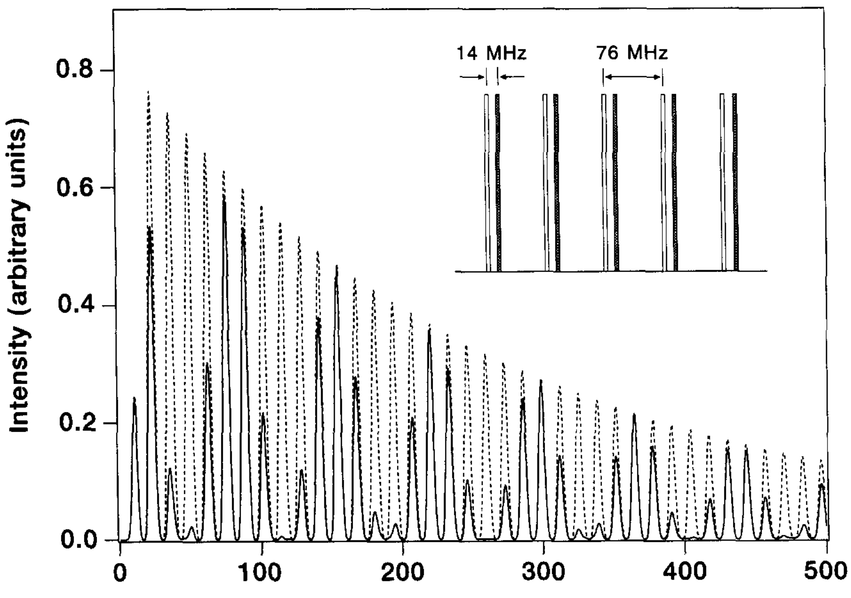

Fig. 4. Theoretically predicted ring-down waveforms for two different model spectra. The dotted curve represents a case where a comb of longitudinal modes with identical spacing of 76 MHz is assumed; the solid curve shows the case where an additional comb separated from the first one by 14 MHz is excited. The parameters in detail are: $\lambda = 3.2$ μm, $L = 0.41$ m, 99% mirror reflectivities and a FWHM pulse duration of 4 ns.

decay envelopes from which meaningful ring-down spectra are easily extracted.

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