The superposition principle and cavity ring-down spectroscopy

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Cavity ring-down is becoming a widely used technique in gas phase spectroscopy. It holds promise for further important extensions, which will lead to even more frequent use. However, we have found widespread confusion in the literature about the nature of coherence effects, especially when the optical cavity constituting the ring-down cell is excited with a short coherence length laser source. In this paper we use the superposition principle of optics to present a general and natural framework for describing the excitation of a ring-down cavity *regardless* of the relative values of the cavity ring-down time, the input pulse coherence time, or the dephasing time of absorption species inside the cavity. This analysis demonstrates that even in the impulsive limit the radiation inside a high finesse cavity can have frequency components only at the natural resonance frequencies of the cavity modes. As an immediate consequence, a sample absorption line can be detected only if it overlaps at least one of the cavity resonances. Since this point is of particular importance for high resolution applications of the technique, we have derived the same conclusion also in the time domain representation. Finally, we have predicted that it is possible to use this effect to do spectroscopy with a resolution much higher than that of the bandwidth of the excitation laser. In order to aid in the design of such experiments, expressions are derived for the temporal and spatial overlap of a Fourier transform limited input Gaussian beam with the TEM_{mn} modes of the cavity. The expressions we derive for the spatial mode overlap coefficients are of general interest in applications where accurate mode matching to an optical cavity is required. [S0021-9606(96)01847-8]

I. INTRODUCTION

In the last few years, cavity ring-down spectroscopy (CRDS) has been applied with increasing frequency to a number of problems, allowing highly sensitive absolute absorption measurements of weak transitions or rarefied species.[1–8] Very briefly, CRDS uses pulsed laser excitation of a stable optical cavity formed by two or more highly reflective mirrors. One observes absorption by molecules contained between the mirrors at the laser wavelength by the decrease it causes in the decay time of photons trapped in the cavity. Absorption equivalent noise as low as $\sim 3 \cdot 10^{-10}/\mathrm{cm}\sqrt{\mathrm{Hz}}$ has been demonstrated, and in principle, several orders-of-magnitude-further-improvement is possible.[3,6]

In several of the recent publications on this subject, we have detected a diffuse belief that the behavior of an optical cavity under impulsive excitation (as in CRDS) is to be considered radically different from that in presence of continuous wave (cw) radiation. This impression has been confirmed by direct discussion with different authors. The purpose of this paper is to clarify the situation by presenting a rigorous analysis of the excitation of an optical cavity that is valid over the full range of parameters that are likely to be of importance in CRDS. Further, the framework introduced here may be useful in the design of new experiments.

The problem can be summed up as follows. Time domain and frequency domain representations of the dynamics of physical systems having linear response are mathematically equivalent, since they are uniquely mapped into each other by a Fourier transformation. Given this equivalence, one is free to choose the most convenient description for the problem at hand, as the final results will not depend on this choice. However, the frequency representation has the general advantage that the spectrum of the ''output'' of a passive device can be simply written as a system response function times the spectrum of the ''input.'' In contrast, the general time domain system response must be expressed as a convolution integral of the input with a time dependent system response function. For an optical cavity, ''input and output'' are the electromagnetic fields arriving from the optical source and going towards the detector, respectively. In CRDS, one may have to deal with input laser pulses that are short compared to the light round trip time inside the cavity. In this limit, it is clear that destructive interference phenomena among the different time components of the injected light should be negligible. More simply, after a pulse is partially transmitted through the cavity input mirror, it does not spatially overlap or interfere with itself as it ''rings down'' inside the cavity. Therefore, it might appear more convenient to use the time domain representation to treat CRDS. It turns out that the frequency domain analysis of the light fields inside and transmitted by a ring-down cavity is quite simple and of general scope. No restrictive assumptions on the pulse duration and bandwidth, the absorbing transition linewidth, or the cavity quality factor are required. For the case of nar-

row absorption lines (which have long dephasing times), the frequency domain analysis is substantially easier than treating time dependent response functions and sample reradiation as would be required for a proper time domain treatment. One of the conclusions of this analysis is that no absorption is possible even in the short pulse limit when the frequency of a narrow absorption feature falls between two cavity modes. For complementarity we also give a (less general) time domain treatment of this important problem, which obviously reaches the same conclusions. This result was previously obtained by Zalicki and Zare,[9] but then recently contested by Scherer *et al.*[7]

The only simple but powerful principle to be applied in the frequency domain analysis is that of linear superposition of the effects produced by the different frequency components in the incoming field.[10] We will show that the standard spectral response function of an etalon can be applied regardless of the temporal profile of the input field. While we expect that many readers will find this result to be so obvious as to not require an explicit derivation, the CRDS literature is rife with statements that contradict this view. Since the comblike structure of this response function reflects the presence of cavity resonances, the cavity mode structure can be considered as a fixed characteristic of the system, and not as something that builds up only if the excitation coherence time is sufficiently long compared to the cavity optical round trip time, as stated in several recent publications. One must be careful not to confuse interference in the time and in the frequency domain. Even if the pulse injected into the cavity is such that its time components do not overlap and interfere, the multiple reflections from the cavity mirrors still result in destructive interference for those frequency components of the pulse which do not overlap any cavity resonances and constructive interference of those that do. Correct predictions of the cavity behavior in different situations follows naturally if one thinks in terms of the cavity resonances in frequency space and the associated spatial mode structure (longitudinal and transversal) in physical space.

Contrary to what has been suggested in the CRDS literature, one of the most interesting consequences of our considerations is that it is possible to turn the high finesse mode structure of the ring-down cavity to a tremendous advantage. We will show that one can use CRDS with a spectral resolution much higher than that of the pulsed laser source. In order to aid in the design of such experiments, expressions are derived for the temporal and spatial overlap of a Fourier transform limited input Gaussian beam with the TEM_{mn} modes of the cavity.

A note is warranted about the application of linear response theory to CRDS. As it has already been noted,[8] even in presence of intense and short laser pulses, nonlinear effects such as the saturation of molecular transitions are usually negligible in CRDS. This is principally due to the strong attenuation of the input laser pulse upon transmission of the cavity input mirror. We would like, however, to warn that there may exist special conditions in which nonlinear effects may become relevant, specifically for very strong transitions and a ring-down cavity employing mirrors of substantial transmittivity (as in the uv). In such cases, one must go beyond linear response theory and the superposition principle should be used with caution.

II. THE SPECTRUM OF LIGHT INSIDE AND TRANSMITTED BY A MODE MATCHED RING DOWN CAVITY

Consider a ring-down cavity (RDC) formed by two mirrors with radius of curvature R_c, separated by a distance L (which must be $<2R_c$ to have a stable cavity[12]). We define $t_r=2L/c$, the round trip time of the cell, where c is the speed of light in the medium between the mirrors. For simplicity, we will assume that the mirrors have identical electric field reflectivity $-\mathscr{R}$ and transmittivity $\mathscr{T}$. The results derived below are easily generalized to the case of assymetric cavities and the results are qualitatively the same. If the mirrors were infinitely thin, continuity of the electric field would give the relationship $\mathscr{R}+\mathscr{T}=1$ between these complex quantities.[11] The reflections and transmitions of the multiple surfaces inside dielectric mirrors can be combined (with propagation phase and absorption) into a single effective frequency dependent $\mathscr{R}$ and $\mathscr{T}$ (an application of the superposition principle), as long as one is outside of the region of the coating. However, this treatment will not yield a continuous electric field, since this solution is not appropriate inside the mirror coatings where one is beyond some surfaces and before others. The more familiar intensity reflectivity and transmittivity are given by $R=|\mathscr{R}|^2$ and $T=|\mathscr{T}|^2$. For now, we will assume that we can treat $\mathscr{R}$ and $\mathscr{T}$ as constants over the bandwidth of input radiation to the RDC. Let us consider excitation of the RDC by light of arbitrary electric field $E_i(t)$, as measured at the input mirror of the cavity. We will also initially assume that the radiation is mode matched to the TEM_{00} mode of the cavity. In these conditions the transverse beam profile is stationary and we can treat the problem as one dimensional along the cavity optical axis z. Below, we will consider the effects of excitation of higher order transverse modes. We can calculate the electric field of light leaving the cavity by adding up all paths that lead to output, which make 1, 3, 5, etc., passes through the cell. The light making one pass has an amplitude of $\mathscr{T}^2E_i(t-t_r/2)$ at time t. Each additional round trip through the cell changes the amplitude by a factor of $\mathscr{R}^2$ and leads to an additional retardation of t_r. Summing the contribution of the possibly infinite number of passes leads to the intracavity electric field, $E(z,t)$ at position z and the output electric field, $E_o(t)$ (measured outside the output mirror at $z=L$),

$$E(z,t)=\sum_{n=0}^{\infty}\mathscr{T}\mathscr{R}^{2n}E_i\left(t-\frac{z+2nL}{c}\right)-\mathscr{T}\mathscr{R}^{2n+1}E_i\left(t-\frac{2(n+1)L-z}{c}\right), \tag{1}$$

$$E_o(t)=\sum_{n=0}^{\infty}\mathscr{T}^2\mathscr{R}^{2n}E_i(t-(n+\tfrac{1}{2})t_r). \tag{2}$$

We can calculate the spectrum (in the angular frequency ω) of this field by computing the Fourier transform (FT). For light transmitted by the cavity we have

$$\begin{aligned}\tilde{E}_o(\omega) &= \frac{1}{\sqrt{2\pi}}\int E_o(t)\exp(-i\omega t)dt \\ &= \frac{1}{\sqrt{2\pi}}\int \sum_{n=0}^{\infty} \mathscr{T}^2\mathscr{R}^{2n}E_i(t-(n+\tfrac{1}{2})t_r) \\ &\quad \times\exp(-i\omega t)dt \\ &= \sum_{n=0}^{\infty} \mathscr{T}^2\mathscr{R}^{2n}\exp(-i(n+\tfrac{1}{2})\omega t_r)\tilde{E}_i(\omega) \\ &= \mathscr{T}^2\exp\left(-\frac{i}{2}\omega t_r\right)\tilde{E}_i(\omega)\sum_{n=0}^{\infty}[\mathscr{R}^2\exp(-i\omega t_r)]^n, \\ \tilde{E}_o(\omega) &= \frac{\mathscr{T}^2\exp\left(-\frac{i}{2}\omega t_r\right)}{1-\mathscr{R}^2\exp(-i\omega t_r)}\tilde{E}_i(\omega).\end{aligned} \tag{3}$$

Above, $\tilde{E}_i(\omega)$ is the FT of the input radiation. The output spectral density, $I_o(\omega)$, of this light is proportional to $|\tilde{E}_o(\omega)|^2$, which gives

$$I_o(\omega) = \frac{T^2}{(1-R)^2+4R\sin^2(\frac{1}{2}\omega t_r-\theta)}I_i(\omega). \tag{4}$$

In this expression, $\theta=\arg(-\mathscr{R})$, i.e., the phase shift per reflection of the mirrors. Going through the same analysis for light inside the cavity, starting from $E(z,t)$ we find

$$I(\omega,z) = T\frac{(1-\sqrt{R})^2+4\sqrt{R}\sin^2(k(L-z)-\theta)}{(1-R)^2+4R\sin^2(\frac{1}{2}\omega t_r-\theta)}I_i(\omega), \tag{5}$$

where $k=\omega/c$ is the wave vector of the light. This shows that for a fixed ω or monochromatic input field, light traveling in both directions inside the cavity leads to standing waves with near nodes in the limit that $R\sim 1$. The time averaged total intensity at z is given by $\int I(\omega,z)d\omega$. For excitation of the cavity with a pulse short compared to t_r, whose bandwidth will be larger than $\sim 1/t_r$, this integral will wash out the standing waves except close to the mirrors.

The above equations are essentially identical to the expression for the transmission of an etalon found in standard optics texts, such as that of Born and Wolf (Ref. 13, page 327). The output spectrum is equal to the input spectrum times a transmission function. For a $R\sim 1$, this intensity transmission function versus frequency consists of a series of narrow peaks with full width at half maximum (FWHM) given by $\Delta\nu_{FW}=(1-R)/(\sqrt{R}\pi t_r)$, separated by the free spectral range, $FSR=1/t_r$, of the etalon. The finesse of the etalon is defined by the ratio of the FSR to the FWHM and is equal to $(\pi\sqrt{R})/(1-R)$. While Eq. (4) is usually derived by considering an infinite wave of pure frequency, it should be noticed that we have made no assumption as to the shape of $E_i(t)$, and thus the input can have any pulse length or coherence time (either short or long compared to t_r). This is, of course, a straightforward consequence of the superposition principle of linear optics, which states that the optical throughput at each frequency can be calculated separately, and is independent of any other spectral components of the wave.[13]

In their recent paper, Scherer *et al.*[7] make the claim ''it seems intuitively more reasonable that the onset of coherent effects should explicitly depend upon the coherence length of the light, since if the phase of the overlapping light is not preserved, a regular interference will not necessarily occur. These results underscore the complexity associated with predicting the behavior of optical resonators which are injected with pulsed laser light, and the subsequent limitation of applying cw–based model to the pulsed regime.'' The derivation presented above demonstrates that this claim is inconsistent with the superposition principle of optics. The coherence length of the input pulse appears in our analysis as part of $\tilde{E}_i(\omega)$ and only affects the relative excitation of different resonance modes of the cavity.

The following considerations might help to further clarify pulsed excitation of an etalon. In the case of an impulsive $E_i(t)$ shorter than t_r, it is clear that there is no destructive interference of the temporal components of the pulse. This is the case if dispersion effects are not sufficiently strong to make the pulse duration become longer than t_r before the pulse is completely decayed. However, absorbing molecules inside the cavity do not see a single pulse, but also its recurrent reflections, with a well defined and constant period t_r. Here, we neglect fluctuations of the cavity length, which is a good approximation if we consider that a typical optical dephasing time, T_2, is much shorter than mechanical vibrations. It is this strict recurrence that produces coherence effects if the molecular transition T_2 is longer than t_r. In the frequency domain, we have shown that, due to the recurrences, the spectrum of the injected light is modulated and this modulation is mathematically represented by multiplication of the initial spectrum by the comblike transfer function of the cavity.

If we were to select a single one of the pulses in the cavity ring-down, say by using a fast electro-optic switch, it would have the same spectrum as the input radiation under the assumptions made above. Of course, such a switch must change its transmission on a time scale less than t_r, and thus will introduce a spectral broadening greater than the spacing between cavity modes of the RDC. The etalon comblike filter convoluted with the spectral broadening produced by the switch will just reproduce a highly attenuated version of the input pulse spectrum. Notice that since the optical switch is a time dependent system, it cannot be represented in frequency space by simple multiplication by a spectral response function, but by a convolution operation.

The fact that a series of equally spaced decaying replicas of the same pulse has a spectrum which is different from that of the single initial generating pulse, is a consequence of the properties of the FT. The fact that this frequency spectrum contains resonances which are closely the harmonics of the

fundamental $1/t_r$ is borne out by the rigorous application of the superposition principle given above, but may be also understood in simpler (though less general) terms as follows. If $t_r \ll t_d$ and we neglect the phase shift per reflection, the repeating pulse is well approximated as a product of an exponential decaying envelope $\exp(-t/2t_d)$ times a periodic function $f(t)$ with period t_r. It is a well known property of periodic functions that they can be decomposed in a Fourier series as $f(t)=\Sigma_{m=-\infty}^{+\infty} f_m \exp(2\pi i m t/t_r)$. Therefore, we find again that only harmonics of the base frequency $1/t_r$ must be present. The effect of the decay is to add a finite Lorentzian width to these resonances. This is seen in mathematical terms by taking the FT of the product $f(t)\times \exp(-t/2t_d)$ and recognizing that this equals the convolution of the individual FT's of each operand (Faltung theorem). The FT of an exponential decay is a Lorentzian, while the FT of the sum of circular functions $\exp(2\pi i m t/t_r)$ is a sum of delta functions $\delta(\omega-2\pi m/t_r)$. The convolution then gives a sum of Lorentzians whose center frequencies are the harmonics of $1/t_r$, which is a good approximation to the comblike cavity transmission function in Eq. (4) in the above limit of $t_r \ll t_d$.

If one looks at the field in the direction of the reflection from the cavity, one will find both the direct reflection of the input pulse plus a pulse train lasting a time t_d that comes from intracavity radiation re-transmitted by the input mirror. In computing the spectrum of this pulse, there will be destructive interference for those spectral components of the input pulse which are resonant with those of the re-transmitted pulse train, leading to ''holes'' in the spectrum of the reflected light. This is of course a natural consequence of the need to separately conserve energy for each spectral component.

Let us now relax the assumption that $\mathscr{R}$ and $\mathscr{T}$ are frequency independent, and allow for the presence of an absorbing medium inside the cell with an absorption coefficient given by $\alpha(\omega)$ and index of refraction given by $n(\omega)$. In principle, we could repeat the above calculation directly in the time domain, but then we would need to consider the time dependent response functions of the mirrors and the re-radiation by the molecules (Ref. 14, p. 490). However, as long as we remain in the linear response limit, we can exploit the superposition principle to look at the reflection and absorption of each spectral component separately, which are just complex multiplicative factors. Adding up the multiple paths for each spectral component, we find the following for the spectrum of light transmitted by the cavity

$$R_{\mathrm{eff}}(\omega)=R(\omega)e^{-\alpha(\omega)L},$$

$$k(\omega)=\frac{n(\omega)\omega}{c},$$

$$\tilde{E}_o(\omega)=\frac{\mathscr{T}^2 e^{-\alpha L/2}e^{-ikL}}{1-\mathscr{R}^2 e^{-\alpha L}e^{-ik2L}}\tilde{E}_i(\omega)=\sqrt{2\pi}\tilde{G}(\omega)\tilde{E}_i(\omega), \tag{6}$$

$$I_o(\omega)=\frac{T^2 e^{-\alpha L}}{(1-R_{\mathrm{eff}})^2+4R_{\mathrm{eff}}\sin^2(kL-\theta)}I_i(\omega), \tag{7}$$

where we have introduced the ''spectral'' Green function $\tilde{G}(\omega)$ (FT of the usual time dependent Green function) for the frequency response of the cavity. For the spectrum of light inside the cavity we have instead

$$I(\omega,z)=T\frac{[1-\sqrt{R}e^{\alpha(z-L)}]^2 e^{-\alpha z}+4\sqrt{R}e^{-\alpha L}\sin^2(k(L-z)-\theta)}{(1-R_{\mathrm{eff}})^2+4R_{\mathrm{eff}}\sin^2(kL-\theta)}\times I_i(\omega). \tag{8}$$

In order to determine the time dependent intensity of light transmitted by the cavity, which is the quantity measured in CRDS, we must compute the inverse FT of $\tilde{E}_o(\omega)$. Using the convolution or Faltung theorem, this can be expressed in the following standard form:

$$E_o(t)=\int G(t-t')E_i(t')dt', \tag{9}$$

where $G(t-t')$ is the Green's function, which represents the cavity response to a delta function input. For the ring-down cavity, this can be written from the expression above as follows:

$$G(t)=\frac{1}{2\pi}\int \frac{\mathscr{T}^2 e^{-\alpha L/2}e^{-ikL}}{1-\mathscr{R}^2 e^{-\alpha L}e^{-ik2L}}e^{i\omega(t)}d\omega. \tag{10}$$

In this integral, one should keep in mind that α, k, $\mathscr{R}$, and $\mathscr{T}$ are all functions of the integration variable ω. We wish to point out that up to this point in the analysis we have made no assumptions beyond linearity of optical response, which is implied by the use of $n(\omega)$ and $\alpha(\omega)$, and the superposition principle of optics.

As long as the width of each absorption line is much greater than the width of the individual resonances (i.e., the T_2 for the optical transition is short compared to t_d), each resonance of the cavity will still have a Lorentzian shape. For realistic parameters at optical frequencies, the transit time broadening of molecules through the narrow TEM_{00} cavity mode will greatly exceed the width of the resonances (but it will be much narrower than their separation). The Lorentzian resonance shape implies that the decay of intensity emitted from the cavity, following impulsive excitation of a single mode, will be exponential. We point out that this limit is violated in Balle–Flygare-type FT microwave spectroscopy, which is conceptually similar to cavity ring-down, but where typically the T_2 due to transit time is long compared to the cavity decay time.[15]

In this limit of cavity resonances much narrower than the interval over which the other frequency dependent terms in the expression for the response function change, we can integrate over each resonance separately. By expanding the exponential $\exp(-ik2L)$ to first order around each ω_q where $k(\omega_q)L=\pi q+\theta$, we get a sum over Lorentzian amplitude terms for which the inverse FT can be computed. The resulting expression is

$$G(t)=\frac{1}{\sqrt{2\pi}}\sum_q A(\omega_q)\exp\left(-\frac{t-t_r/2}{2t_d(\omega_q)}\right)\times\exp[i\omega_q(t-t_r/2)]\Theta(t-t_r/2), \tag{11}$$

where $\Theta(x)$ is the step function ($=1$ or 0 for $x>0$ or <0, respectively) and

$$t_d(\omega_q)=\frac{t_r R_{\rm eff}}{2(1-R_{\rm eff})}, \tag{12}$$

$$A(\omega_q)=\sqrt{2\pi}\frac{\mathcal{T}^2 e^{-\alpha L/2}}{t_r R_{\rm eff}}, \tag{13}$$

with $R_{\rm eff}(\omega)$ and $k(\omega)$ as defined above. Note that due to the small but finite propagation delay through the cavity, causality requires that $G(t)$ is zero for $t<t_r/2$ rather than just for $t<0$.

Equations (9) and (11) demonstrate that the requirement on the input source to observe a cavity ring-down is not that its pulse width be short compared to t_r, or even t_d, but only that the falling edge of the input pulse be short compared to $t_d(\omega_q)$ for the modes q that are significantly excited. Those modes will be determined by the spectrum of the input radiation, and (when we consider the effect of higher transverse modes below) the spatial properties of the radiation. However, for a typical pulsed laser the total extent in time of the input radiation is itself much shorter than the cavity decay times. In this impulsive limit, we can neglect the exponential cavity decay during the input pulse, and if we place the time origin at the input pulse, we can explicitly evaluate the integral in Eq. (9) using Eq. (11) to give

$$E_o^{\rm imp}(t)=\sum_q A(\omega_q)\exp\left(-\frac{t-t_r/2}{2t_d(\omega_q)}\right)\times\exp(i\omega_q(t-t_r/2))\tilde{E}_i(\omega_q), \tag{14}$$

for times greater than the end of the input pulse plus $t_r/2$. The result is a sum of damped exponential decays for each cavity resonance. Since the electric field has a decay lifetime of $2t_d$, the intensity in each mode has decay lifetime of t_d. The decay rate, and thus the spectral width, of those resonances which overlap the sample absorption spectrum will be increased. Sample absorption lines that do not overlap excited cavity modes do not contribute to the rate of light intensity decay and are not detectable in CRDS.

If we treat $n(\omega)$ and $\theta(\omega)$ as changing slowly with ω (thus neglecting dispersion effects due to narrow absorption lines), the cavity mode spacing is given by

$$\mathrm{FSR}=\frac{c}{2L\left(n(\omega)+\omega\frac{dn}{d\omega}\right)-c\frac{d\theta}{d\omega}}. \tag{15}$$

For constant $dn/d\omega$ and $d\theta/d\omega$, we have equally spaced resonance modes. If in addition $R_{\rm eff}$ is constant, the pulse in the cavity travels with no change in shape since the effective loss and group velocity is the same for all frequencies contained in its bandwidth. Dispersion changes the velocity of the wave due to both the $\omega(dn/d\omega)$ term, which is standard (Ref. 10, p. 302), and the $d\theta/d\omega$ term which reflects that different wavelengths have different average penetration into the optical coating of the mirrors and thus travel different pathlengths. The effective t_r is given by 1/FSR [where FSR is now defined by Eq. (15)] for a cavity with dispersion. If we consider the contribution to $n(\omega)$ by the sample absorption, we see that this will slightly increase the index and thus decrease the mode spacing on the low frequency side of a transition, and the opposite on the high frequency side. Zalicki and Zare[9] suggested that dispersion effects are generally negligible for the weak absorption strengths investigated by CRDS. We agree with this if one is observing only the decay of energy in the cavity, as is typically done, since in this case the interference between different excited modes is filtered out. However, if one attempts to model the time dependent shape of the train of peaks leaving the cavity, then the small shifts in resonance frequency caused by dispersion must be considered along with the frequency dependent absorption. We have explicitly shown by numerical calculation, using Eq. (14) for the case of a Lorentzian absorption line narrow compared to the input pulse, that the cavity output displays the expected sample free induction decay *after* the excitation pulse, only if these shifts in resonance frequencies are included in the calculation. This is an interesting subject for future investigation[16] since changes in pulse shape may be useful for extracting information about the sample absorption spectrum on frequency scales between the linewidth of the laser used to excite the RDC and the spacing between longitudinal cavity modes.

Scherer *et al.* state in their paper[7] that, ''In the case of simple exponential decay, the cavity does not act as an etalon, i.e., standing waves are not established in the cavity.'' On the contrary, exponential decay is a natural consequence of the RDC being a high finesse etalon, if it is excited on a single cavity mode. More typically, we have multiple mode excitation, due both to the bandwidth of the excitation source and due to lack of exact transverse mode matching. As discussed by Zalicki and Zare,[9] for multiple mode excitation we expect in general a multiple exponential decay of the RDC unless the excited modes have the same loss $R_{\rm eff}$. Even in this case, the intensity of the decay will not be exactly exponential, but show modulations due to beating between different mode frequencies. Beating among longitudinal modes (same transverse mode numbers) will have periods that are submultiples of t_r. This simply corresponds to the exponentially decaying series of pulses generated by the initially injected light as it rings down inside the cavity. Thus a simple exponential decay of the cavity implies that only one longitudinal mode has been excited, which also requires that a standing wave must be produced inside the cavity, in direct conflict with the above statement of Scherer *et al.* In most applications of CRDS, however, the difference between t_r and t_d is large enough that this round-trip beating pattern can be easily filtered electronically without significantly distorting the exponential signal envelope which is the sum of the decay of each excited cavity mode.

III. CAVITY RING DOWN WITH A NARROW BANDWIDTH ABSORBER

The paper by Zalicki and Zare[9] considered the effect of having an intracavity absorption feature with a linewidth narrower than the bandwidth of the laser used to excite the cavity. As long as one is exciting many modes of the cavity across the absorption line, this leads to nonexponential cavity decay. This has been verified by Jongma *et al.*[17] and more quantitatively by Hodges *et al.*[18] These effects are closely related to the well known line shape distortions observed in conventional absorption spectroscopy when the instrumental resolution is not higher than the width of spectral features. There, the observed sample absorption (integrated over the instrument function) does not follow Beer's law for samples that are optically thick.[19] For optically thin samples, such measurements give the correct integrated line strength (also known as the equivalent width), though not the correct peak value due to instrumental broadening of the line. Hodges *et al.*[18] have demonstrated that an additional complication can arise in cavity ring-down due to the spectral structure in conventional multimode pulsed lasers. This results in intensity distortions when the width of an absorption feature is comparable to the width of structures in the spectrum of the excitation laser. We anticipate that these effects can be removed by averaging ring-down decays observed as the modes of the excitation laser are swept to produce a smooth average excitation line shape.

Another important consideration discussed by Zalicki and Zare is the relationship between the width of the absorption features and the FSR of the cavity. They report to show that the bandwidth of light admitted into the RDC depends upon the length of the excitation pulse. We think that this is a consequence of their considering the FT only over a time interval of the input pulse (which they took to have a square wave amplitude) and not of the whole damped series of reflections the intracavity molecules interact with. Despite this, they recognize that the excitation caused by the coherent sum of all the cavity reflections will only excite transitions that overlap one of the excited modes of the RDC. Thus they reach the same observable consequence as the present analysis and one may dismiss the differences in our respective analysis as largely semantic.

In a frequency domain analysis of the problem, one should integrate (in calculating the FT) over the whole time of interaction. To consider the spectral content of the radiation field only in a given limited time interval is equivalent to employ a mixed time frequency representation. Time and frequency localized representations are the subject of wavelet transform theory, which is becoming quite an active field of research and application in recent years.[20]

It is often useful to compare descriptions of the same phenomena both in the time and frequency domains, though they must give the same results. The analysis we will present below is also complimentary in that it focuses on the molecules in the cavity, while the earlier treatment focused on the optical properties of the system. Consider excitation of a two level system with optical resonance ω_0 and dipole matrix element for the transition μ_{21}. Let the molecule be at position z_0 at $t=0$ and its velocity along the axis of the RDC be v_z. Starting with Eq. (8.1–6) in the text by Yariv,[12] and then using first order time dependent perturbation theory, we find that the coherence between the two states, ρ_{21}, created by the time dependent electric field is given by

$$\rho_{21}(t)=e^{-i\omega_0 t}\frac{i}{\hbar}\int_{-\infty}^{t}\mu_{21}E(z_0+v_z t',t')e^{i\omega_0 t'} \times(\rho_{11}-\rho_{22})_{\mathrm{e}}dt', \tag{16}$$

where $(\rho_{11}-\rho_{22})_{\mathrm{e}}$ is the equilibrium difference in populations between the lower and upper levels of the optical transition. We will assume that the input pulse is shorter than one round trip time, t_{r}. This is done only for simplicity. In fact, we could divide any arbitrary incoming field in portions that are shorter than the round trip time, and the following analysis could be applied to each of these ''time components'' and the results added. We will use Eq. (1) for $E(z,t)$ for the field inside the RDC.[21] Putting this into the above equation, we find for the coherence induced by the pulse

$$\rho_{21}(t)=e^{-i\omega_0 t}\sum_{n=0}^{\mathrm{int}(t/t_{\mathrm{r}})}\left\{\rho_+ R^n e^{-i2n\theta}\exp\left[i\omega_0\left(1+\frac{v_z}{c}\right)nt_{\mathrm{r}}\right] -\rho_- R^{n+1/2}e^{-i(2n+1)\theta}\exp\left[i\omega_0\left(1-\frac{v_z}{c}\right)(n+1)t_{\mathrm{r}}\right]\right\}, \tag{17}$$

where $\rho_\pm$ is the coherence produced by a single forward or reverse going pulse in the cavity

$$\rho_\pm=\frac{i}{\hbar}\mu_{21}\sqrt{T}(\rho_{11}-\rho_{22})_{\mathrm{e}}\exp\left(\pm i\omega_0\frac{z_0}{c}\right) \times\int E_{\mathrm{i}}^{*}(t)\exp\left(i\omega_0\left(1\pm\frac{v_z}{c}\right)t\right)dt. \tag{18}$$

We will get constructive interference (and thus net absorption) of the coherence produced on successive round trips of the cavity only if ω_0 satisfies the following equation with integer N

$$\omega_0\left(1\pm\frac{v_z}{c}\right)=\frac{2\pi}{t_{\mathrm{r}}}N+\frac{2\theta}{t_{\mathrm{r}}}. \tag{19}$$

Thus we will only get net absorption by the sample if either the forward or backward Doppler shifted Bohr frequency (the left hand side of the above equation) satisfies the same equation as a cavity resonance [see Eq. (4)]. The cavity acts to produce a multiple-pulse time domain ''Ramsey'' fringe pattern, as previously noted by Zalicki and Zare.[9] Including a T_2 for the optical transition will allow off resonance absorption, but this is just equivalent to considering the resulting line broadening in the frequency domain. Thus we recover the condition that CRDS is only sensitive to sample absorp-

tion that overlaps one of the very narrow cavity resonances excited by the input radiation, even in the limit of short pulse excitation.

The spectral selectivity of sample excitation inside a RDC can be shown to be demanded also by the laws of thermodynamics. Let us suppose, contrary to what we have demonstrated above from first principles, that the RDC does not act as an etalon for short pulse (or short coherence length) excitation, and that the full bandwidth of the pulse enters the cavity and excites all optical transitions that overlap its spectrum, as is claimed by Scherer *et al.*[7] It has been experimentally demonstrated that spontaneous emission is turned off in a cavity with no mode resonant with the atomic transition.[22] If black body radiation could enter the cavity and excite an atom, but the atom were not able to undergo spontaneous emission, an infinite atomic electronic temperature would be produced by interaction with a finite temperature heat bath. This clearly would be a violation of the second law of thermodynamics.

The fact that the RDC acts as a frequency selective filter might lead to the erroneous conclusion that CRDS is not suitable for quantitative spectroscopy of high resolution spectra. This is simply not the case. As Meijer *et al.*[5] have shown, the excitation of many transverse modes of the RDC will lead to a near continuous spectrum of cavity resonances, eliminating this potential problem. We will return to this point below. At present, we will show how even with single mode excitation of the RDC cell, one need not miss absorption features.

The narrow bandwidth of light admitted into a RDC offers a tremendous opportunity for high resolution spectroscopy. One has to replace the static length cell considered by Meijer *et al.*, Zalicki and Zare, and others, by a cell whose length can be varied by at least $\lambda/2$, (one-half wavelength) which will shift each mode by one FSR of this ''etalon.'' Since only light with a bandwidth much narrower than the excitation laser enters the cell, it is possible to do spectroscopy with a resolution much greater than that of the laser source used to excite the cavity! Consider a commercially available OPO laser with a bandwidth of $\sim$125 MHz. By using a cavity of length $L<75$ cm, the mode spacing will be greater than twice the laser linewidth and if mode matched, we will primarily excite only one mode. We can then scan the cavity and observe a spectrum with a full width instrumental resolution of $\sim$16 kHz for a cavity decay time of $\sim 10\ \mu$s. In practice, time of flight of molecules through the laser beam will limit resolution to about 0.1 MHz, 3 orders of magnitude better than the FT limit for a few nanoseconds laser pulse. Such experiments will require interferometric control of the length of the RDC, and tracking the excitation laser as the cavity is scanned. The latter should be of minor difficulty, since in this situation, high contrast interference fringes will be observed as the cavity and laser are detuned, allowing for standard feedback techniques to be used. Maintaining the RDC to interferometric accuracy, say $\sim$1 MHz, can, in principle, be achieved in several ways. One can purchase a temperature stabilized etalon with such passive stability, which could be modified to act as a cell for CRDS. By using a continuous wave laser locked on a molecular transition, one could also lock the RDC to a spectroscopic standard. Since we can repetitively scan the cavity over one FSR and observe the time when the reference laser passes through resonance, we can have continuous feedback control of the cavity length. In this case, one can use the time that the excitation laser is fired relative to the scanning ramp to control the frequency sampled on any laser shot.

Thus rather than being a problem, the frequency selective nature of the cavity resonances opens the possibility for a dramatic improvement in the resolution available in pulsed laser experiments. The combination of this technique with CRDS should dramatically improve both the sensitivity and resolution that can be realized in sub-Doppler spectroscopy.

While this work was being reviewed for publication, we were informed of an earlier experiment that demonstrated these principles. Teets *et al.*[23] observed a two-photon transition in atomic sodium inside an optical cavity of modest ($\approx$16) finesse. By scanning the length of the cavity, they observed a transition of width 12 MHz, despite a Fourier transform limit for the input pulse of about 170 MHz. The round trip time of the cavity used (13 ns) was about twice the length of the input pulse. The spectral selectivity observed in this experiment directly invalidates the model of CRDS presented by Scherer *et al.*[7]

The next section will consider the spectrum of longitudinal modes excited by a FT limited pulse having Gaussian transverse profile. We also need to account for the fact that without great care, one will excite multiple transverse modes of the cavity, each of which has its own resonance frequency. The following section will then consider the excitation of higher transverse modes.

IV. FRINGES VERSUS THE EXCITATION PULSE LENGTH

Consider the mode matched excitation of a RDC by a pulse with center frequency ω_c. For a sufficiently short input, this excitation will create a traveling pulse inside the RDC. Neglecting dispersion effects, this pulse will propagate back and forth with no change in intensity profile, except for a slow attenuation. If dispersion effects are important over the bandwidth of the pulse, either from spectral changes in mirror reflectivity and phase shifts, or from the presence of a narrow absorption feature that is not optically thin, the intracavity pulse shape will change with time. In a frequency domain picture, this corresponds to the variable mode spacings described by Eq. (15).

The most obvious sign that the cell is acting as an etalon would be the observation of ''fringes'' in the transmitted light as the center frequency of the excitation beam is scanned. It is the lack of such a modulation when the input pulse is short compared to t_r that appears to have produced the belief that a RDC does not act as an etalon in the impulsive limit. However, it is well known that one does not observe interference fringes if one excites an etalon with broad bandwidth light. This is just a consequence of the transmission spectrum being periodic with period equal to the FSR.

Thus if the input pulse spectrum is much wider than one FSR, the expected interference structure is ''washed out,'' and the transmission coefficient becomes constant with value $T^2/2(1-R)$, independent of the center frequency of the input light pulse.

What happens if the input pulse length is closer to the value of the cavity round trip time? Zalicki and Zare considered this question for the case of square wave excitation.[9] We presently consider a FT limited Gaussian shaped input pulse with an intensity FWHM equal to Δt, since this provides a better model for many real lasers. The frequency spectrum of this input pulse will also be Gaussian, with a FWHM equal to $0.44/\Delta t$ (Ref. 24 p. 334). In the limit of a high finesse RDC, each resonance will have a nearly Lorentzian shape with peak transmission equal to $[T\exp(-\alpha L/2)/(1-R_{\text{eff}})]^2$, and FWHM equal to $1/2\pi t_{\text{d}}$, where $t_{\text{d}}=n(\omega_q)L\sqrt{R_{\text{eff}}}/[c(1-R_{\text{eff}})]$ is the decay time for the qth resonance mode and $R_{\text{eff}}=R\exp(-\alpha(\omega_q))$ is the effective reflectivity for that mode.

Cavity resonances will be narrow relative to the spectral structure of the input pulse as long as the pulse duration is short compared to t_{d}. Therefore, in order to calculate the total intensity transmitted by the cavity, we can treat the resonances as delta functions. This approximation will break down, because of the long tails of the Lorentzian resonances, when the width of the input pulse is much narrower than cavity mode spacing, i.e., when $\Delta t \gg t_{\text{r}}$. For each resonance mode q at frequency ω_q, from Eq. (4) we find that the energy transmitted by the cavity is

$$J_q = J_0\sqrt{\frac{\pi}{\ln 2}}\,\frac{\Delta t}{t_{\text{r}}}\,\frac{T^2}{2(1-R)} \times\exp\left[-\left(\frac{\pi}{\sqrt{\ln 2}}\,\frac{\Delta t}{t_{\text{r}}}\,\frac{(\omega_q-\omega_c)}{\text{FSR}}\right)^2\right], \tag{20}$$

where J_0 is the energy in the input pulse. The total transmitted energy is obtained by summing over all the resonance modes. In the limit that the input pulse is short compared to t_{r} the sum over modes can be approximated by an integral which gives just the factor of $T^2/2(1-R_{\text{eff}})$ expected for incoherent excitation of an etalon. In Fig. 1, we plot the ratio of the predicted transmission divided by this incoherent excitation value for the pulse center frequency exactly resonant with a cavity mode and for when it is exactly halfway between cavity modes. The ratio of the two curves is the expected fringe modulation as the excitation laser (or the RDC length) is scanned. Significant modulation is observed when Δt is greater than $\sim 0.5t_{\text{r}}$. This can be rationalized when one remembers both that the Gaussian has a tail and is not a square wave (where there would be zero modulation for $\Delta t < t_{\text{r}}$) and also that interference is given by overlap of the electric field, which has a FWHM $\sqrt{2}\Delta t$. When one recalls that for a Gaussian pulse $\Delta t\Delta\nu = 0.44$, we see that when the FWHM of the pulse is half the cavity round trip time, the spectral width has a FWHM only 0.88 as large as the spacing between the longitudinal modes. When the laser pulse is centered on a mode, the ratio of the mode excitation to that of its next neighbors is given by $\exp[-(\pi\Delta t/\sqrt{\ln 2}t_{\text{r}})^2]$. When $\Delta t = 0.5t_{\text{r}}$, this ratio is already only 0.028, while for $\Delta t = t_{\text{r}}$, this ratio is $6.6\,10^{-7}$. Thus very selective excitation of a transverse mode matched RDC is possible with FT limited pulses with FWHM of $\sim 0.5t_{\text{r}}$ or longer. Below, we will see that the need for mode matching can be relaxed in case of a confocal (or more generally re-entrant) cavity configuration.

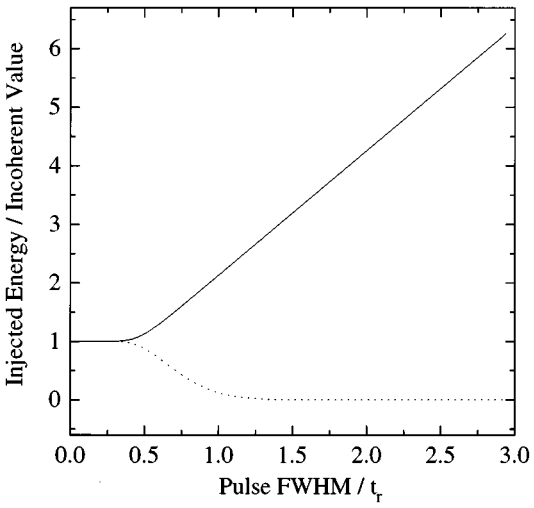

FIG. 1. Plot of the ratio of the predicted transmission divided by its incoherent excitation value for the pulse frequency centered on a cavity mode (solid line) and for when it is halfway between cavity modes (dashed line).

V. EFFECT OF HIGHER ORDER TRANSVERSE MODES

Our analysis up to this point has been one dimensional, which is appropriate for light perfectly mode matched into the RDC. In order to consider the excitation of a RDC produced by a beam with an arbitrary spatial distribution, we must again use the superposition principle, but now in space rather than time, expanding the input wave in a set of cavity modes. Due to the finite transverse extent of an open optical cavity, its resonances, unlike those of the closed electromagnetic cavities commonly treated in textbooks, need not be a complete, orthogonal set (Ref. 24, p. 568). However, stable cavities with small diffraction losses have resonance modes closely approximated by Hermite–Gauss functions up to relatively high transverse mode orders, which do have this attractive property (Ref. 24, p. 569). We will derive the general cavity output, for an arbitrary input pulse, by expansion in both frequency (for the time dependence) and cavity modes (for the transverse spatial dependence). While the following discussion is for the response of the cavity calculated at its output, the same treatment can be applied to the field produced inside the cavity and leads to similar results.

In the paraxial approximation (small propagation angles and deviations from the optical axis), the Maxwell equation for wave propagation in a homogeneous dielectric medium [refraction index $n(\omega)$] has a set of solutions known as the transverse electro–magnetic (TEM) modes,[12,24] whose order

is indexed by two positive integers (m,n). The spatial field amplitude for these modes is written in terms of Hermite–Gauss functions

$$\mathscr{E}_{mn}(x,y,z,\omega)=\frac{1}{\sqrt{2^{m+n-1}\pi n!m!w^2(z)}}H_m\left(\frac{\sqrt{2}x}{w(z)}\right)\times H_n\left(\frac{\sqrt{2}y}{w(z)}\right)\exp\left(-\frac{x^2+y^2}{w^2(z)}-\frac{ik(x^2+y^2)}{2R_{\rm f}(z)}-ikz+i(m+n+1)\eta(z)\right). \tag{21}$$

These monochromatic waves have wave vector $k=n(\omega)\omega/c$ along z, and time dependence $\exp(i\omega t)$. They are characterized by a transverse beam waist of size $w(z)$, by a radius of curvature of the phase fronts $R_{\rm f}(z)$, and by a phase shift induced by diffraction $\eta(z)$. For free space propagation along the paraxial axis z, these TEM parameters change as follows:

$$w(z)=w_0\sqrt{1+\left(\frac{z-z_w}{z_0}\right)^2},$$
$$R_{\rm f}(z)=(z-z_w)\left[1+\left(\frac{z_0}{z-z_w}\right)^2\right], \tag{22}$$
$$\eta(z)=\arctan\left(\frac{z-z_w}{z_0}\right),$$

with z_w the focal point of the wave, where the beam waist reduces to its minimum w_0. Once the value of w_0 is given, the ''confocal length'' z_0 is also determined

$$z_0\equiv\frac{\pi w_0^2 n(\omega)}{\lambda}. \tag{23}$$

At fixed frequency ω, fixed w_0 (or equivalently z_0) and fixed $R_{\rm f}$ (or z), the set of TEM$_{mn}$ modes form a complete orthogonal and normalized set of functions

$$\int \mathscr{E}^*_{m'n'}(x,y,z,\omega)\mathscr{E}_{mn}(x,y,z,\omega)dxdy=\delta_{m'm}\delta_{n'n}, \tag{24}$$
$$\sum_{m,n}\mathscr{E}^*_{mn}(x',y',z,\omega)\mathscr{E}_{mn}(x,y,z,\omega)=\delta(x'-x)\delta(y'-y).$$

In the axially symmetric case, each mode is degenerate with respect to polarization.

If we wish to consider light coupled into an optical cavity made of two mirrors, then one should select the beam parameter so that the radius of the beam just matches the radius of curvature of each mirror at its surface. For the symmetric cavity considered in here (both mirrors with curvature R_c, as before), this condition implies that the beam focus is at the center of the cavity and the confocal length is[12]

$$z_0=\tfrac{1}{2}\sqrt{(2R_c-L)L}. \tag{25}$$

More general expressions can be found in the text by Yariv.[12] The condition that z_0 is real defines the range of stable symmetric cavities $L<2R_c$. While z_0 for the TEM set of cavity modes is frequency independent, note that this is not the case for $w_0^2=\lambda z_0/\pi n(\omega)$.

We now consider an input field of angular frequency ω that has a spatial distribution that just matches the TEM$_{m,n}$ mode of the field. We denote the amplitude of this field by $\tilde{E}_{{\rm i},mn}(\omega)$. Similar to the one dimensional case [Eq. (7) and following], we can sum over all round trips through the cavity to arrive at an output electric field, which will still match the TEM$_{m,n}$ in the perpendicular plane and have an amplitude given by

$$\tilde{E}_{{\rm o},mn}(\omega)=\sqrt{2\pi}\tilde{G}_{mn}(\omega)\tilde{E}_{{\rm i},mn}(\omega), \tag{26}$$

where

$$\tilde{G}_{mn}(\omega)=\frac{1}{\sqrt{2\pi}}\frac{\mathscr{T}^2e^{-\alpha L/2}e^{-ikL}}{1-\mathscr{R}^2_{mn}e^{-\alpha L}e^{-i(k-\delta k_{mn})2L}}, \tag{27}$$

$$\delta k_{mn}L=2(m+n+1)\arctan\sqrt{\frac{L}{(2R_c-L)}}. \tag{28}$$

The different transverse amplitude distribution of each TEM mode may result in different losses due to spatially varying defects in the mirrors surfaces and to their finite size. We account for this by using mode dependent reflectivities $\mathscr{R}_{mn}(\omega)$.

Like in the one dimensional case, $\tilde{G}_{mn}(\omega)$ is a comblike transmission function, and we can identify the longitudinal cavity resonances with the peaks of this function, and their decay rate with their width. The functional dependence of $\tilde{G}_{mn}(\omega)$ is similar to that for the one dimensional case of Eq. (7), but the position of its resonances has a shift dependent on the TEM order, due to the $\eta(z)$ term in Eq. (21). The frequencies of the longitudinal resonances are found by the solutions of the following equation (obtained numerically by iteration)

$$\omega_{mnq}=\frac{c}{n(\omega_{mnq})L}\left[\pi q+\theta+2(m+n+1)\times\arctan\sqrt{\frac{L}{(2R_c-L)}}\right], \tag{29}$$

where θ is the phase change upon reflection, introduced earlier. In the time domain, each mode will have an exponential decay with a time constant (for power) given by

$$t_{{\rm d},mn}(\omega_{mnq})=\frac{t_{\rm r}R_{mn,\rm eff}}{2(1-R_{mn,\rm eff})} \tag{30}$$

with $R_{mn,\rm eff}=R_{mn}\exp(-\alpha(\omega_{mnq})L)$. Note that if $R_{mn}(\omega)$ is not constant due to mode dependent loss, we will have a nonexponential decay even without sample absorption.

We will now consider excitation of a cavity by an arbitrary input pulse whose electric field is given by $E_{\rm i}(x,y,z,t)$. Using the superposition principle, we can expand $E_{\rm i}(x,y,z,t)$ in terms of the set of functions $\mathscr{E}_{mn}(x,y,z,\omega)$ for which we have just presented the transmission properties. The total output field, $E_{\rm o}(x,y,z,t)$ can then be written as

$$E_o(x,y,z,t)=\sum_{mn}\int \tilde{G}_{mn}(\omega)\tilde{E}_{i,mn}(\omega)\mathscr{E}_{mn}(x,y,z,\omega)e^{i\omega t}d\omega, \tag{31}$$

where $\tilde{G}_{mn}(\omega)$ is given by Eq. (27) and

$$\tilde{E}_{i,mn}(\omega)=\frac{1}{\sqrt{2\pi}}\int\int\int \mathscr{E}^*_{mn}(x,y,z,\omega) \times E_i(x,y,z,t)e^{-i\omega t}dx\ dy\ dt. \tag{32}$$

$\tilde{E}_{i,mn}(\omega)$ is the ''excitation amplitude'' of the mode with transverse order mn and frequency ω. Note that we do not have to specify at which value of z the integral is evaluated at, due to the superposition principle for space propagation.

If we assume that the input field has a small fractional bandwidth, which allows one to neglect the frequency dependence of the TEM parameters, we can derive another expression for the time dependent cavity output decomposed over the spatial TEM modes. For each mode, the cavity response is then a convolution of the corresponding Green function with the time dependent amplitude $E_{i,mn}(t)$ for that mode[25]

$$E_o(x,y,z,t)=\sum_{mn}\mathscr{E}_{mn}(x,y,z,\omega')e^{ik(\omega')z} \times\int G_{mn}\left(t-t'-\frac{nz}{c}\right)E_{i,mn}(t')dt', \tag{33}$$

where ω' is the center of the field bandwidth; $G_{mn}(t)$ is the inverse Fourier transform of $\tilde{G}_{mn}(\omega)$ given by Eq. (27); and $E_{i,mn}(t)$ is the inverse Fourier transform of $\tilde{E}_{i,mn}(\omega)$.

We leave to Appendix A the discussion of some special cases and examples. An important case is that of a beam which is separable as the product of space and time dependent functions. A special separable case is when the spatial component of the beam is Gaussian and astigmatic, with arbitrary spot sizes, focal positions and axis, but only slightly tilted with respect to z as required by the paraxial approximation. Then, recursive analytic expression exist and are derived in Appendix B for the amplitude excitation coefficients in terms of the beam parameters. These results allow one to model the coupling of a laser operating on a single TEM_{00} mode to an external optical cavity. In addition, the method of the Appendix B can be extended to input beams with higher TEM order, and the expressions derived could be applied to the more general case of a beam which is the superposition of TEM modes characterized by the same arbitrary parameters. This would be adequate for modeling the cavity coupling of a nonseparable beam produced by a laser which is not operating on a single transverse mode.

Let us consider the case when for each mn the longitudinal resonances in $\tilde{G}_{mn}(\omega)$ are narrow with respect to other spectral widths of the problem. In the time domain this implies that the variation of the field is faster than the cavity decay times. Then, the same result as in Eq. (11) can be obtained here and Eq. (14) can be generalized to

$$E_o(x,y,z,t)=\sum_{m,n,q}A_{mn}(\omega_{mn})\tilde{E}_{i,mn}(\omega_{mnq})\mathscr{E}_{mn}(x,y,z,\omega_{mnq}) \times\exp\left[i\left(t-\frac{t_r}{2}\right)\omega_{mnq}\right]\exp\left(-\frac{t-t_r/2}{2t_{d,mn}}\right), \tag{34}$$

where the factor $A_{mn}(\omega)$ is given by Eq. (13) with $R_{eff,mn}$ in place of R_{eff} and $t_{d,mn}$ is given by Eq. (30). For brevity, the dependence on ω_{mnq} has been left implicit for several of the parameters. The output intensity of the cavity will contain beating between different excited modes. However, if one detects the total light intensity crossing the output plane, the orthogonality of the mode functions eliminates beats between modes with different transverse mode numbers.

The fraction of input pulse energy coupled to a particular TEM_{mn} mode is given by the squared magnitude of the mode overlap amplitude, $|E_{i,mn}|^2$, times a spectral density factor, which for the case of an input pulse with Gaussian temporal profile was given by Eq. (20), which is easily generalized to the present case. Thus together with the results of Appendix B, we have given explicit expressions for the distribution of excitation of different modes of an optical cavity for an input pulse of Gaussian shape in space and time, with alignment restricted by the paraxial conditions and of duration short compared to the cavity decay time. The present results can be easily extended, using numerical integration, to treat input pulses of arbitrary temporal and spatial shape.

As seen by Eq. (34), the output signal in CRDS is only sensitive to the sample loss at the frequencies of excited modes of the cavity, and thus the spectrum of the cavity is important to the design and interpretation of CRDS. We can see that the longitudinal modes (for fixed m,n) are separated by angular frequency $2\pi/t_r$, while transverse modes (changing $m+n$, with q fixed) are separated by $(4/t_r)\times\arctan\sqrt{L/(2R-L)}$. The full spectrum of the cavity (say for an incoming plane wave that excites all TEM orders) will be continuous if the ratio of these spacings is irrational. If it is rational with the transverse spacing to the longitudinal spacing equal to M/N, the spectrum will consist of a series of resonances with frequencies exactly spaced by $1/(t_rN)$, i.e., exactly a factor of N less than the separation of the TEM_{00} modes. It is easily seen from above that for a confocal cavity ($L=R_c$), the transverse mode separation is exactly half of the longitudinal modes, giving a frequency spacing between resonances of $1/2t_r$. However, for other values of the spacing we can get other low order rational ratios. For example, if $L=R_c/2$ or $3R_c/2$, we will get a frequency spacing of $1/3t_r$, i.e., just 3 times as dense as the TEM_{00} modes.

For general multiple mode cavity excitation, the transverse profile of the light intensity changes shape on each pass of the cell. For a rational ratio as discussed above with divisor N, the intensity will be exactly periodic (except for an overall damping factor) after N round trips. This is the separation condition for the multipass re-entrant cavity configurations used and discussed by Herriott *et al.*[26]

Meijer *et al.*[5] suggested that one could use a nonconfocal

cavity to achieve an essentially continuum excitation spectrum and thus eliminate the expected distortions of the cavity ring-down spectrum caused by a static cell acting as a frequency filter. They used slightly diverging input radiation (incorrect sign of R_f compared to the mode matched case) to insure that a wide range of transverse modes were excited, giving a dense spectrum. We would like to point out that one must be careful not to inadvertently use a mirror separation that leads to a rational ratio unless the divisor is large enough that the resulting ''picket fence'' spectrum has spacings much smaller than the linewidths in the spectrum one wishes to observe.

We would also like to mention that the clever solution of Meijer *et al.*[5] comes at a cost of reduced spatial resolution in CRDS. This is clearly undesirable when the method is used, as by Zalicki *et al.*,[8] to observe the spatial profile of a species' concentration. A perhaps more general problem is that it increases the required size and spatial uniformity of the coatings of mirrors used for CRDS. A multiexponential ring-down signal will result from excitation of modes with different transverse profile if the different portions of the mirrors surfaces have different reflectivity. Such variations in reflectivity may be caused also by dust or dirt. Further, changes in the distribution of modes excited as the laser is scanned will lead to variations in the ''background'' loss of the cell which will translate into a poor zero absorption baseline. It is also important to ensure that the entire cross section of the beam is collected and detected to prevent transverse mode beating from distorting the cavity ring-down. We wish to emphasize that these are surmountable issues in most experiments, but they should be considered in experimental design.

The experiments described by Scherer *et al.*[7] have been interpreted by them as demonstrating that a RDC does not act as an etalon even for input pulses with a FWHM twice as long as the cavity round trip time. They base this in part on the lack of modulation in the observed cavity transmission as a function of the center frequency of their near transform limited laser. As is shown in Fig. 1, very strong fringe modulation is expected for a transverse mode matched cavity when the input pulse length is as long as twice the cavity round trip time. However, these authors make no mention in their paper of any attempt to mode match the radiation, nor to carefully adjust the mirror separation for a re-entrant configuration. Thus it is almost certain that the reported lack of fringe modulation is a consequence of the effects previously predicted by Meijer *et al.*[5] The interference structure has been ''washed out'' due to simultaneous excitation of many TEM_{mn} cavity modes. This also naturally accounts for the fact that they observed a methane spectrum with the same relative intensities and linewidths when observed with different length cavities, even though the longitudinal mode spacing of the shorter cavity was almost twice the observed FWHM of the methane lines. Scherer *et al.* claim that their results contradict the analysis of Zalicki and Zare.[9] The present work demonstrates that the experimental results of Scherer *et al.* are completely in accord with the prior predictions of Meijer *et al.*, and in no way contradict the results of Zalicki and Zare. The same conclusion has been reached by Hodges, Looney, and van Zee.[27] In a series of careful measurements, they have recently verified that CRDS cells have the expected etalon transmission properties even when excited with laser pulse length a few times the cavity round trip time, directly contradicting the claims of Scherer *et al.*

For certain applications of cavity ring-down, especially for obtaining spectral resolution higher than the input laser, the mode coupling, or cavity mode structure, or both, will have to be carefully controlled. Mode matching requires control over four experimental variables: (1) The position of the input beam relative to the optic axis of the etalon; (2) the relative input angle; (3) the spot size; and (4) the radius of curvature. Precise adjustment of the first two is a routine part of most optical setups and is easily optimized. Control of the second two requires the equivalent of a ZOOM telescope lens. In addition, if the laser source is not operating on a stable TEM_{00} mode, spatial filtering will be needed to obtain a Gaussian beam profile that can be matched to the cavity TEM_{00} mode. Monitoring the size and shape of the intensity emitted from the cavity, say with a camera,[18] appears to provide a direct diagnostic to allow the optimization of the input coupling. The *Super Cavity*, a high finesse spectrum analyzer sold by Newport Co., uses a near planar cavity ($L \ll R_c$); in our laboratory we have achieved $>90\%$ excitation of the TEM_{00} mode of such a cavity by using a GRIN lens at fixed distance from the cavity to focus the output of a single mode fiber.[28] One can thus expect high selectivity with careful alignment of a near diffraction limited beam, which for most pulsed lasers will require spatial filtering. Likely, it will be more convenient to use a confocal or another ''degenerate'' mirrors separation. Note, however, that a confocal cavity is unstable if one has any finite difference in the curvature of the two cavity mirrors![12,24] The precision required for the mirror separation will increase linearly with both the number of transverse modes excited and with the ultimate resolution required. We note that for exactly coaxial excitation of the cavity with a symmetric beam, one will only get excitation of TEM_{mn} modes with even values of m and n, and thus have an effective transverse mode spacing twice what is otherwise expected.

Thus in applications of CRDS one is often interested in either deliberately exciting a known range of cavity modes or in carefully exciting only the lowest order one. It is then useful to have expressions for the excitation of different modes expected for a given input beam. In Appendix B, we give an analytic expression for the overlap of a Gaussian input beam with arbitrary parameters and alignment with respect to the TEM_{00} mode of the cavity, and a recursion relationship that allows the overlap with higher order modes to be calculated as well. These general formulae are sufficiently complex that it is difficult to directly gain insight by inspection of the results, though they can be easily programmed and plotted for different ranges of parameters. In Appendix A limiting examples are considered that will likely be useful estimating precision needed for a specific experimental arrangement.

We wish to close this section with a brief discussion of diffraction effects in optical cavities used in CRDS. The

quantitative theory of these effects is rather complicated and we refer the reader to the text by Siegman[24] for a good introduction to this subject; the material given below is taken from this source. It is interesting that the simple first order estimate of mode losses, by calculation of the fraction of a given Gaussian mode that ''spills over'' the mirrors, substantially overestimates the diffraction losses. The low order resonant modes distort (''pull in their skirts''), falling below the Hermite–Gaussian function near the mirror edge, thereby effectively reducing diffraction losses. Diffraction losses are typically characterized by the dimensionless resonator Fresnel number, $N_f=a^2/(L\lambda)$, where $2a$ is the diameter of the resonator limiting aperture (usually the mirror coating), L is the cavity length, and λ the wavelength of resonant light. Values of $N_f\sim 100$ are common in CRDS experiments. For a stable cavity not far from a confocal design, the highest order Gaussian modes that will ''fit'' inside the cavity aperture will have $m,n\approx \pi N_f$. Given the rapid fall-off of the Hermite–Gaussian functions beyond their ''classical turning points,'' diffraction losses fall rapidly for modes with m,n below this limiting value. For the TEM_{00} mode of a confocal cavity with circular mirrors, the single pass diffraction power loss is approximately $\pi^2 2^4 N_f \exp(-4\pi N_f)$ for $N_f>1$. This represents a loss of $\sim 4\times 10^{-52}$ even for $N_f=10$!

VI. CONCLUSION

We have demonstrated that contrary to widespread belief coherence effects are important in cavity ring-down spectroscopy in presence of narrow absorption lines, independent of the physical or coherence length of the laser pulse used to excite the cavity. We find that the superposition principle of optics provides a natural and convenient framework for predicting the effects of cavity excitation, regardless of the spectral or spatial characteristics of the light source. Using the frequency domain representation we have shown that for mirrors of high reflectivity the radiation field inside the cavity will have negligible spectral intensity outside the cavity resonances. This gives a simple and general solution to the problem of absorption lines narrower than the cavity free spectral range, since it indicates that absorption will be observable only when the lines overlap the cavity resonances. We have shown that the same can also be obtained in the time domain representation by using first order time dependent perturbation theory to account for the total molecular excitation produced as an input light pulse bounces back and forth through the cavity. The problem of missing absorption lines in cavity ring-down measurements has been previously considered,[5,9] but we have here discussed in more detail the advantages and possible limitations of the proposed solution of using high order cavity mode excitation. In addition, we have argued that the frequency selectivity of a ring-down cavity can be turned in a tremendous advantage, opening the possibility of using this technique to observe spectra with a resolution much higher than that of the excitation laser. Finally, we have derived general analytic expressions for calculating the transverse mode expansion amplitudes of an arbitrary input Gaussian beam that is coupled into an optical cavity.

While ring-down cavity spectroscopy is a technique that yields good results with a very simple setup, a thorough understanding of the properties of resonant cavities is necessary for optimal design of the experiment and for this technique to be used for quantitative absorption measurements of spectra with narrow lines.

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APPENDIX A: TRANSVERSE CAVITY MODE EXPANSION

A good approximation if the input radiation derives from a laser operating on a single transverse mode, is that the beam has a separable space and time dependence, $E_{is}(x,y,z)E_{it}(t)$. Then, if we assume that the TEM parameters do not change appreciably over the (limited) bandwidth of the input field, we can deal explicitly with the fast ω dependent term $(\exp(-ikz))$ in the TEM functions and find that the projection coefficients are also separable

$$\begin{aligned}\tilde{E}^{sep}_{i,mn}(\omega)&=\tilde{E}_{it}(\omega)e^{i(k-k')z}\int E_{is}(x,y,z)\mathscr{E}^*_{mn}(x,y,z,\omega')dx\,dy\\&=E_{is,mn}\tilde{E}_{it}(\omega)e^{i(k-k')z},\\E^{sep}_{i,mn}(t)&=E_{is,mn}E_{it}\left(t+\frac{zn}{c}\right),\end{aligned}\tag{A1}$$

where the $E_{is,mn}$ are practically constants, and $k'=k(\omega')$. Using these results, one can write somewhat simpler expansions in TEM modes for the cavity response

$$E^{sep}_o(x,y,z,t)=\sum_{mn}E_{is,mn}\mathscr{E}_{mn}(x,y,z,\omega')\times\int\tilde{G}_{mn}(\omega)\tilde{E}_{it}(\omega)e^{iwt}d\omega\tag{A2}$$

$$=\sum_{mn}E_{is,mn}\mathscr{E}_{mn}(x,y,z,\omega')e^{ik'z}\times\int G_{mn}(t-t')E_{it}(t')dt'.\tag{A3}$$

We will now consider two special cases which we believe will be helpful in selecting experimental parameters.

First, we would like to consider the case of input radiation with the same spot size and curvature as those of the cavity TEM_{00} mode, but having its propagation axis misaligned by an angle of θ_x with respect to the cavity axis, and displaced by a distance of x_0 in the focal plane of the cavity. We assume the angular and displacement misalignments are in the xz plane. Using the analogy to a harmonic oscillator, this is equivalent to initial preparation of a Glauber coherent state[31,32] with dimensionless phaser, α, given by

$$\alpha = \frac{1}{\sqrt{2}}\left(\frac{x_0}{w_0} - ikw_0 \sin\theta_x\right). \tag{A4}$$

This state will be a superposition of a Poisson distribution of TEM_{m0} modes, with mean value $|\alpha|^2$ and a standard deviation equal to the square root of the mean, or $|\alpha|$. Thus to strongly excite a range of $\sim K$ modes, we either need to displace the input beam $\sim K$ spot sizes off the optic axis, or misalign the input angle by $\sim K/kw_0$. For excitation of a large number of modes, this result will be insensitive to small changes in the spot size or radius of curvature away from the mode matched values.

As a second special case, we consider excitation with a Gaussian beam aligned with the optic axis of the cavity, but with input values for the spot size, w_x, and radius of curvature, R_x, that may not match those, w and R_f, of the cavity modes. In this case, we get for the overlap with the TEM_{00} mode of the cavity the amplitude, $E_{i,00}$ [see Eq. (B6)],

$$E_{i,00} = \frac{2ww_x}{w^2 + w_x^2 + \frac{i}{2}kw^2w_x^2\frac{R_f - R_x}{R_xR_f}}. \tag{A5}$$

The only higher order modes that will have nonzero overlap are those with even values for both m,n. The magnitude of these overlaps will decrease approximately exponentially with $m+n$ [see Eq. (B14)], with the width of the distribution being $\sim 2/E_{i,00}$.

APPENDIX B: GENERAL MODE OVERLAP AMPLITUDES

We wish to give general expressions for the TEM expansion amplitudes $\tilde{E}_{i,mn}(\omega)$ of an arbitrary input Gaussian beam that is coupled into an optical cavity. This problem is mathematically closely related to the calculation of electronic Franck–Condon factors in the harmonic approximation. Below we give a derivation that exploits a method one of the authors developed for that problem.[33] Recently, we became aware of two previous publications that reported mode ''coupling coefficients.'' The first was an article by Kogelnik[29] which provided general close form expressions for the case of a perfectly aligned cavity, but only presented results for the coupling to the lowest order mode in the case of a misaligned input beam. Bayer–Helms[30] presented results with arbitrary misalignment as well as input mode mismatch. The resulting expressions, however, are rather complex and appear much more difficult to use than the simple recursion relationships given below. Further, neither of these previous works dealt with the case of a cavity or input beam with astigmatism, which is easily treated by the present approach.

The z axis of our coordinate system is defined by the optical axis of the cavity. For the case of a symmetric cavity, the origin of the coordinate system is located at its center. We will pick an arbitrary xy plane (a fixed value of z) to compute the overlap integrals, where the cavity TEM modes are characterized by the spot size $w(z)$, radius of curvature $R_f(z)$, and phase $\eta(z)$ given in Eqs. (22) together with Eqs. (23) and (25). These TEM_{mn} modes can be separated as products of two components, $\mathscr{E}_m(x)$ and $\mathscr{E}_n(y)$ [see Eq. (21)], with

$$\mathscr{E}_m(x) = \frac{\sqrt[4]{2/\pi}}{\sqrt{2^m m!\, w}} H_m\left(\frac{\sqrt{2}x}{w}\right) \times \exp\left(-\frac{x^2}{w^2} - \frac{ikx^2}{2R_f} - \frac{i}{2}kz + i\left(m+\frac{1}{2}\right)\eta\right). \tag{B1}$$

For the input beam, we will assume a generic free space elliptic Gaussian beam.[12] In the paraxial approximation, the axis of this beam will have tilt angles θ_x and θ_y in the x and y directions. We will take the origin of the beam coordinate system at the point $(x_{00}, y_{00}, 0)$ of the cavity coordinate system. By writing the overall tilt as a product of a rotation θ_x around the y axis and then by θ_y around the rotated x axis, and using the paraxial approximation of small angles, one can write the transformation from the beam coordinates x', y', z' to the cavity coordinates like this

$$\begin{aligned} x' &\simeq x\cos\theta_x - z\sin\theta_x - x_{00} \simeq x - z\sin\theta_x - x_{00}, \\ y' &\simeq y\cos\theta_y - z\sin\theta_y - y_{00} \simeq y - z\sin\theta_y - y_{00}, \\ z' &\simeq x\sin\theta_x + y\sin\theta_y + z\cos\theta_x\cos\theta_y. \end{aligned} \tag{B2}$$

Applying this transformation to the elliptic Gaussian beam function $E(x',y',z')$ in Eq. (6.12–8) of Yariv,[12] we can then separate it as a product of two terms, $E_x(x)$ and $E_y(y)$, which we normalize for integration on the xy plane. The x component is

$$E_x(x) = \frac{\sqrt[4]{2/\pi}}{\sqrt{w_x}} \exp\left(-\frac{(x-x_0)^2}{w_x^2} - \frac{ik(x-x_0)^2}{2R_x} - ikx\sin\theta_x - \frac{i}{2}kz\cos\theta_x\cos\theta_y + \frac{i}{2}\eta_x\right), \tag{B3}$$

where the beam parameters w_x, R_x, and η_x are functions of z' as for the TEM modes parameters of Eqs. (22). However, we have to approximate $z' \simeq z$ in the argument of these parameters, which is necessary for the evaluation of the overlap integrals below. Taking into account also the position z_{wx} of the beam waist in the xz plane, we have therefore

$$w_x(z)=w_{x0}\sqrt{1+\left(\frac{z-z_{wx}}{z_{x0}}\right)^2},$$

$$R_x(z)=(z-z_{wx})\left[1+\left(\frac{z_{x0}}{z-z_{wx}}\right)^2\right], \tag{B4}$$

$$\eta_x(z)=\arctan\left(\frac{z-z_{wx}}{z_{x0}}\right), \quad x_0(z)=x_{00}+z\ \sin\ \theta_x,$$

where $x_0(z)$ is the beam displacement in the x direction. The confocal parameter is related to the beam waist w_{x0} as usual, $z_{x0}=\pi w_{x0}^2 n(\omega)/\lambda$. Analogous equations can be written for the $E_y(y)$ function, with different parameters w_{y0}, z_{wy} which allow for astigmatism of the input beam. Finally, notice that the wave number k in this equation is the same as that of the TEM modes we use to evaluate the expansion amplitudes, since we are working in the frequency domain, at fixed ω.

Since we have chosen the mode functions to be normalized with respect to integration over the xy plane, we can calculate the overlap amplitudes $E_{\mathrm{i},mn}$, which give the expansion of the input wave in terms of TEM_{mn} cavity modes, by

$$\tilde{E}_{\mathrm{i},mn}(\omega)=\tilde{E}_{x,m}\tilde{E}_{y,n},$$

$$\tilde{E}_{x,m}=\int \mathscr{E}_m^*(x)E_x(x)dx$$

$$=\frac{1}{\sqrt{2^m m!\,\pi}}\sqrt{\frac{w}{w_x}}\int H_m(\xi)\exp(-a\xi^2-b\xi-c_m)d\xi,$$

$$a=\frac{w^2}{2}\left[\frac{1}{w^2}+\frac{1}{w_x^2}+\frac{ik}{2}\left(\frac{1}{R_x}-\frac{1}{R_f}\right)\right], \tag{B5}$$

$$b=\frac{w}{\sqrt{2}}\left[-\frac{2x_0}{w_x^2}-\frac{ikx_0}{R_x}+ik\ \sin\ \theta_x\right],$$

$$c_m=\frac{x_0^2}{w_x^2}+\frac{ikx_0^2}{2R_x}-\frac{i}{2}kz(1-\cos\ \theta_x\ \cos\ \theta_y)$$

$$+i\left(m+\frac{1}{2}\right)\eta-\frac{i}{2}\eta_x,$$

with an analogous equation for the $\tilde{E}_{y,m}$ terms as integrals over dy. For the case of $\tilde{E}_{x,0}$, we are left with an integral over the exponential term, which is easily solved by completion of squares to put it in standard form. The result is

$$\tilde{E}_{x,0}=\sqrt{\frac{w}{aw_x}}\exp\left(\frac{b^2}{4a}-c_0\right). \tag{B6}$$

Recursion relationships for the higher overlap terms are obtained exploiting the properties of the Hermite polynomials (Ref. 32, p. 531). Using the relationship $H_{m+1}(\xi)=2\xi H_m(\xi)-2mH_{m-1}(\xi)$, it is easy to show

$$\tilde{E}_{x,m+1}=\frac{1}{\sqrt{2^{m-1}(m+1)!\,\pi}}\sqrt{\frac{w}{w_x}}\int \xi H_m(\xi)k_{m+1}(\xi)d\xi$$

$$-\sqrt{\frac{m}{m+1}}e^{-2i\eta}\tilde{E}_{x,m-1}, \tag{B7}$$

where we have introduced for convenience $k_m(\xi)=\exp(-a\xi^2-b\xi-c_m)$, with the simple property $k_{m+1}=\exp(-i\eta)k_m$. Using also $H_m'=2mH_{m-1}$ and integrating by parts, one can show that

$$\int \xi H_m k_m(\xi)d\xi=\frac{m}{a}\int H_{m-1}k_m(\xi)d\xi$$

$$-\frac{b}{2a}\int H_m k_m(\xi)d\xi. \tag{B8}$$

Substituting this into the previous equation, we find the recursion relationship

$$\tilde{E}_{x,m+1}=-\frac{b}{a}\frac{e^{-i\eta}}{\sqrt{2(m+1)}}\tilde{E}_{x,m}$$

$$+\left(\frac{1}{a}-1\right)\sqrt{\frac{m}{m+1}}e^{-2i\eta}\tilde{E}_{x,m-1}. \tag{B9}$$

Since this gives the correct $\tilde{E}_{x,1}$ if we use $\tilde{E}_{x,-1}=0$, one can calculate all $\tilde{E}_{x,m}$ starting from the $\tilde{E}_{x,0}$ given before. If one correctly propagates along z the parameters both of the input beam and of the cavity modes, one can verify that the $E_{\mathrm{i},mn}(\omega)$ coefficients are invariant in value, as expected.

Using these relationships, it is possible to calculate the full set of $\tilde{E}_{mn}$ overlap coefficients for the coupling of an arbitrary input pulse having a Gaussian transverse profile. By a straightforward extension of the present method, the case of an arbitrary input with a Hermite–Gaussian profile (and therefore any linear combination of such profiles) can be handled as well.

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