Cavity ring-down spectroscopy for quantitative absorption measurements

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We examine under what conditions cavity ring-down spectroscopy (CRDS) can be used for quantitative diagnostics of molecular species. We show that CRDS is appropriate for diagnostics of species whose absorption features are wider than the spacing between longitudinal modes of the optical cavity. For these species, the absorption coefficient can be measured by CRDS without a knowledge of the pulse characteristics provided that the cavity ring-down decay is exponential. We find that the exponential ring-down decay is obeyed when the linewidth of the absorption feature is much broader than the linewidth of the light circulating in the cavity. This requirement for exponential decay may be relaxed when the sample absorption constitutes only a small fraction of the cavity loss and, consequently, the sample absorbance is less than unity during the decay time. Under this condition the integrated area of a CRDS spectral line approximates well the integrated absolute absorption coefficient, which allows CRDS to determine absolute number densities (concentrations). We determine conditions useful for CRDS diagnostics by analyzing how the absorption loss varies with the sample absorbance for various ratios of the laser pulse linewidth to the absorption linewidth for either a Gaussian or a Lorentzian absorption line shape. © *1995 American Institute of Physics.*

I. INTRODUCTION

Cavity ring-down spectroscopy (CRDS) is a new laser absorption technique that has the potential for the quantitative detection of atomic and molecular species with a high sensitivity, comparable to photoacoustic spectroscopy. CRDS was first demonstrated by O'Keefe and Deacon in 1988.[1] In CRDS, a laser pulse is stored in a high-finesse optical cavity containing the sample, and the pulse decay is monitored with the aid of a detector that measures the intensity of light transmitted through one of the mirrors. This arrangement allows measurement of the absorption over pathlengths exceeding thousands of times the sample length, in a way that is immune to variations in the light source intensity. To date, CRDS has been successfully applied when the absorption is as small as one part in 10^7 for tasks such as measuring the weak overtone spectra of HCN[2,3] or the absorption spectra of jet-cooled metal clusters.[4] This technique has also been applied to measure the kinetics of phenyl radical reactions,[5,6] the temperature of OH radicals in a flame,[7] and the optical gain in a chemically pumped BiF laser system.[8] Recently, CRDS has been used to determine the absolute transition strengths in the CO molecule[9] and to measure CH_3 radicals in a reactor for diamond film growth.[10]

In an empty cavity formed by mirrors of 99.99% reflectivity with a separation of 0.1 to 1 m, the pulse can be stored for microseconds during which it makes thousands of round trips. The intensity of the pulse decreases exponentially in time with a rate determined by the reflectivity of the mirrors and the length of the cavity. Therefore, by measuring the time constant for the intensity decay of the light stored in a cavity, referred to as the ring-down time τ, the reflectivity of the mirrors can be determined. When the cavity contains an absorbing gas, an additional optical loss occurs which causes a decrease in the ring-down time. By recording how the inverse of the ring-down time varies as a function of frequency of the incident light, the CRDS spectrum of the gas is obtained.

Several authors postulated that light in a cavity filled with an absorbing gas decays exponentially with the ring-down time τ given by[2,5,7]

$$\tau = \frac{t_r}{2[(1-\mathscr{R}) + \alpha l_s]}, \tag{1}$$

where t_r is the round-trip time of a light pulse in the cavity, $(1-\mathscr{R})$ denotes the reflection loss for the cavity mirror of reflectivity $\mathscr{R}$, and $2\alpha l_s$ is the round-trip absorbance for a sample present in the cavity with absorption coefficient α and length l_s. Provided Eq. (1) is valid, a plot of $1/\tau$ as a function of laser frequency gives the absolute absorption coefficient versus frequency, from which the sample's number density (concentration) can be determined with a knowledge of the sample's absorption cross section. As will be shown below, this conclusion is not always correct but is an excellent approximation under cetain conditions. The goal of this paper is to find the conditions for which Eq. (1) holds and can be used to recover complete spectra of absorption coefficient versus wavelength from CRDS measurements.

First, we have to consider conditions that allow for reliable measurement of absorption in the optical cavity. In the general case, the analysis is complicated because of the need to distinguish different time regimes defined by the pulse duration t_p, the relaxation time T_2 of the absorbing species (resulting from both homogeneous and inhomogeneous line broadening mechanisms), the round-trip time t_r, and the cavity ring-down time τ. Typically, the length of the optical cavity varies from 0.1 to 1 m so that the round-trip time t_r varies from 0.7 to 7 ns. Although the temporal output of lasers ranges from femtoseconds to cw, most lasers used in CRDS applications have a pulse duration t_p of 3–15 ns. The time t_p has to be compared to the relaxation time T_2, which can be roughly deduced from the inverse of the HWHM γ of

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the absorption line. For a homogeneous line profile, the exact relation $T_2=1/\gamma$ holds; for a Doppler profile, T_2 is typically in the range of 0.1–1 ns. When $t_p \gg T_2$, the amplitude of the pulse envelope does not change during the relaxation time T_2 so that the species absorption in the cavity can be described under the rate approximation (see Appendix A), similar to the case of absorption of cw light. This rate approximation is well fulfilled as long as T_2 is much shorter than the ring-down time τ. To evaluate an absorption of light inside the cavity under the rate approximation, the spectrum of light must be compared to the absorption linewidth of species inside the cavity. Under the condition that $t_p > t_r$, the interference between pulse fragments propagating in the same direction in the cavity causes the cavity to have longitudinal modes, and the width of these modes narrows as t_p increases. Consequently, absorption occurs when the absorption line overlaps one or more of these longitudinal modes. Hence, we require that the linewidth of the absorbing species is wider than the spacing between longitudinal modes for CRDS to be applicable, i.e., to provide a complete spectrum without missing absorption features. For a pulse duration t_p shorter than t_r, no longitudinal modes of the cavity build up but the absorption line is much wider than the maximum possible longitudinal mode spacing because $T_2 \ll t_p < t_r$.

On the other hand, for $T_2 \gg t_p$, the species inside the cavity are absorbing pulses of light and we must consider the relaxation time T_2 of the absorbing species compared to t_r. When $T_2 \gg t_r$, the species are interacting with a sequence of pulses emerging from the cavity mirrors during the time T_2. The spectrum of such a sequence of pulses is given by the product of a spectrum of a single pulse times the periodic pattern that resembles the cavity longitudinal mode structure. Consequently, the molecules in the cavity do not absorb light except at the frequencies of the cavity longitudinal modes, and it is necessary that the absorption linewidth is wider than the spacing of the longitudinal modes of the cavity for CRDS to be applicable. Under the condition of $T_2 \ll t_r$, which guarantees that the absorption linewidth is wider than the maximum possible longitudinal mode spacing of the cavity, the absorption species effectively see a single pulse during the relaxation time T_2 and simply absorb some fraction from the pulse linewidth.

So far, we have distinguished two limiting cases, when the absorbing species interacts with quasi-cw light during time T_2 ($T_2 \ll t_p$), and when the absorbing species interacts with a pulsed light during time $T_2 (T_2 \gg t_p)$. In both cases it is necessary that the linewidth of the absorbing species is greater than the spacing between the longitudinal modes of the cavity for CRDS to be applicable. We still need to establish under what conditions the ring-down decay is exponential and obeys Eq. (1). In the general case, Eq. (1) is valid when the linewidth of the absorbing species inside the cavity is wider than the linewidth of the light inside the cavity. This condition, which ensures Beer's law for absorption, is common to all kinds of absorption spectroscopies. For CRDS, a weaker condition also holds, namely, an approximately exponential decay occurs when the loss from the absorption by species in the cavity is much less than the total cavity loss. Under this condition an effective absorption coefficient can be measured even though the linewidth of the light inside the cavity is broader than the absorption linewidth. The integral of this effective absorption coefficient over the frequency nearly equals the integrated absorption coefficient.

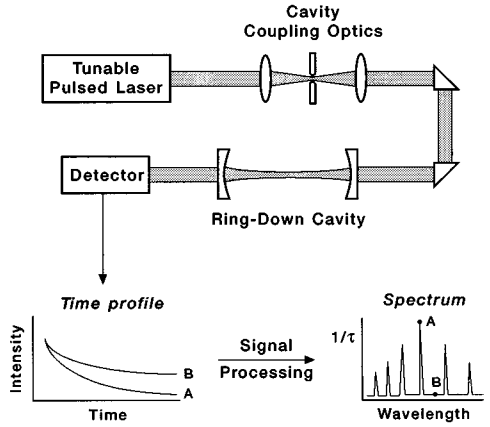

FIG. 1. Schematic diagram of the CRDS experiment.

It what follows, we present the theory for cavity ring-down spectroscopy. In Sec. II, we introduce the principles of the CRDS technique and discuss conditions for absorption of species in the cavity to yield an exponential ring-down decay. A more detailed analysis of this conditions, in association with Beer's law of absorption, is given in Appendix A. In Sec. IV, we introduce conditions where Beer's law fails but the approximately exponential ring-down decay occurs and the integrated absorption coefficient can be still measured by the CRDS technique. The interference effects in the optical cavity and their consequences for species absorption inside the cavity are discussed in Sec. III and Appendix B.

II. PRINCIPLES OF CAVITY RING-DOWN SPECTROSCOPY

Figure 1 presents a schematic drawing of the CRDS apparatus. A typical experiment consists of a pulsed laser source, an optical cavity with coupling optics, and a photodetection system. A stable optical cavity is formed by two concave mirrors of high reflectivity. These mirrors serve also as the side windows of the sample gas cell or of the molecular beam chamber. A laser pulse enters the cavity through one of the mirrors. The pulse is spatially shaped via a pinhole iris to form a TEM_{00} mode of the cavity. It then circulates inside the cavity (reflecting back and forth) with minimum diffraction. For each round trip, the pulse energy decreases because of reflection losses at the mirrors and the absorption by the gas sample between the cavity mirrors.

The decrease of pulse energy is monitored by measuring the intensity of light transmitted through the exit mirror of the cavity as a function of time. The intensity of signal $S(t)$ is given by the product of the intensity of light $I(t)$ at the transmitting cavity mirror times the mirror transmittivity $\mathcal{T}$: $S(t)=\mathcal{T} I(t)$. For a short input pulse, the intensity pattern of the cavity output consists of a train of pulses of decreasing

intensity. If the input pulse length is longer than the cavity round-trip length, these pulses overlap and give a continuous decay waveform.

If more than a single longitudinal mode is excited in the cavity, beats between the modes occur at the cavity output which may cause modulation of the continuous decay waveform. The pattern of mode beats is specific for the longitudinal mode structure built by the laser pulse inside the cavity, and usually changes from pulse to pulse because of the shifts in the relative phase of the modes. Consequently, the beat pattern, if present, washes out significantly after the decay waveform is averaged over several laser pulses.[11]

Consider the decay of light in a cavity containing no sample under the condition where no beats between cavity modes are observed. During a round-trip period t_r (i.e., the time for the light to complete a full round trip in the cavity), the intensity $I(t)$ decreases by the square of mirror's reflectivity $\mathscr{R}$: $I(t+t_r)=\mathscr{R}^2 I(t)$. If the output signal $S(t+nt_r)$ is monitored after n round trips starting from some time t, the signal measured has the form

$$S(t+nt_r)=\mathscr{R}^{2n}S(t),$$
$$=\exp[2n\ \ln(\mathscr{R})]S(t). \tag{2}$$

For $\mathscr{R}$ close to unity, $\ln(\mathscr{R})$ may be approximated by $-(1-\mathscr{R})$ and Eq. (2) becomes

$$S(t+nt_r)=\exp[-2n(1-\mathscr{R})]S(t). \tag{3}$$

We define

$$\mathscr{L}_0=2(1-\mathscr{R}) \tag{4}$$

to be the round-trip loss coefficient for the empty cavity. Then,

$$S(t+nt_r)=\exp(-n\mathscr{L}_0)S(t). \tag{5}$$

Equation (5) resembles Beer's law. We can determine the value of $\mathscr{L}_0$ and the mirror's reflectivity $\mathscr{R}$ by fitting the experimentally observed ring-down waveform to Eq. (5) and using for n the ratio of the observation time $[(t+nt_r)-t]$ to the round-trip period t_r.

When the cavity is filled with an absorbing medium, an extra loss is introduced on each round trip. If Beer's law behavior is valid, this loss is given by the sample absorbance $2\alpha l_s$ where α is the frequency-dependent absorption coefficient of the sample having a length l_s inside the cavity. Hence the round-trip loss coefficient for the cavity with sample becomes

$$\mathscr{L}=2[(1-\mathscr{R})+\alpha l_s]. \tag{6}$$

The CRDS spectrum of absorbance is given as the difference of the cavity loss coefficients: $\alpha l_s=1/2(\mathscr{L}-\mathscr{L}_0)$. Expressing these two loss coefficients by means of the ring-down time $\tau=t_r/\mathscr{L}$ and $\tau_0=t_r/\mathscr{L}_0$, we obtain $\alpha l_s=1/2\mathscr{L}_0(\Delta\tau/\tau)=(1-\mathscr{R})(\Delta\tau/\tau)$.

Consequently, the minimum absorbance measured with the CRDS apparatus is limited by the mirror reflectivity $\mathscr{R}$ and the minimum change in the time τ that can be detected. For mirror reflectivities as high as $\mathscr{R}=99.99\%$ and for the reported accuracy in the ring-down time determination of $(\Delta\tau/\tau)_{\min}=5\times10^{-3}-2\times10^{-3}$,[2,7] the minimum measured absorbance $(\alpha l_s)_{\min}$ is on the order of a few parts in 10^7.

The following conditions, common to all absorption spectroscopies, must be fulfilled for Beer's law behavior to describe absorption of light in the optical cavity (see Appendix A):[12]

—when a cavity contains multiple longitudinal modes, the range of frequencies covered by these modes must be narrower than the absorption line so that the coefficient $\alpha(\omega)$ describing the absorption may be treated as constant over the mode structure frequencies ω.

—for each longitudinal mode being absorbed, the time at which the mode envelope changes must be longer than the relaxation time T_2 characterizing the absorption line.

The above conditions assure that the linewidth of the light in the cavity is narrower than the width of the absorption line. If the linewidth of the light is too broad, i.e., a pulse of too short a length is used or the pulse bandwidth exceeds the width of the absorption line, the loss coefficient $\mathscr{L}$ is not constant as a function of the observation time and nonexponential decay can result.

When Beer's law behavior fails, CRDS can still be used to obtain quantitative information, but the reduction of this information to the absorption spectrum of the sample inside the cavity will require detailed knowledge about the pulse characteristics. Consequently, we emphasize in this paper determining the conditions for which the ring-down waveform shows exponential decay as a function of time.

The following discussion should make the above conclusions more easily understood. Consider as an example the decay of a long, multimode pulse in a cavity. When the pulse linewidth is broader than the width of an absorption line, only those frequencies that are on resonance are absorbed by the sample and attenuated by the mirrors, whereas off-resonant frequencies are exclusively attenuated by the mirrors. This condition in general causes nonexponential decay that requires more than one time constant for adequate modeling.

On the other hand, consider a CRDS experiment accomplished with a single-mode laser pulse. Because only a small fraction of the initial pulse intensity can enter the cavity, pulse absorption can be analyzed analytically by linear, first-order perturbation theory. The problem of absorption of a weak Gaussian pulse of coherent light by a resonant medium was investigated theoretically by Crisp in 1970.[13] He showed that the decrease of pulse intensity with absorption pathlength is described by Beer's law only in the limit that the pulse duration is long compared with the transverse relaxation time T_2 for the medium (including both homogeneous and inhomogeneous broadening). This result was rationalized on the basis of the argument that a pulse of duration comparable to or less than the transverse relaxation time T_2 has a spectral content (linewidth) that is comparable to or broader than the absorption line of the attenuating medium.

In these two examples, the linewidth of the absorption feature was assumed to cover many longitudinal modes of

the optical cavity. We consider next what happens when the linewidth of the absorption feature is comparable to or narrower than the spacing between longitudinal cavity modes.

III. INTERFERENCE EFFECTS IN A CAVITY

The predecessor of the CRDS technique was the work of Anderson, Frisch, and Masser[14] who built a high-sensitivity ring-down reflectometer in which a monochromatic cw laser beam is resonantly coupled with a cavity, and the ring-down decay is monitored after switching off the beam with a fast modulator. O'Keefe and Deacon[1] proposed to measure the ring-down time of the optical cavity with a pulsed laser source, using a pulse whose spatial length or coherence length is shorter than the cavity length. This solution allows for continuous scanning of the laser frequency without jumping from mode to mode as the frequency is scanned. Both approaches, switched cw laser beam or broad-linewidth laser pulse, seem to be suitable for CRDS, As we show, in each case the same limitation for the absorption linewidth holds, namely, the linewidth of the absorption feature must be wider than the spacing between the cavity longitudinal modes.

For laser pulses whose length exceeds the round-trip length $l_r = ct_r$ of the cavity, interference occurs between pulse fragments propagating in the same direction inside the cavity. These interference effects are the subject of the Fabry–Perot theory of resonators. The interference pattern formed in a cavity shows resonance enhancement of intensity for the frequencies interfering "in phase," and quenching of intensity for the frequencies interfering "out of phase." It is this interference pattern that is the source of etalon effects that cause variation of the intensity of light transmitted through a cavity as a function of frequency. The optical frequencies for which the intensity of light inside the cavity is resonantly enhanced give rise to the longitudinal modes of the cavity.

The cavity longitudinal mode structure is defined by the cavity geometry and the pattern of transverse modes sustained in the cavity by the laser pulse. The TEM_{00} transverse mode has longitudinal eigenmodes at frequencies $\omega_m = 2\pi m/t_r$, where t_r is the cavity round-trip time for the TEM_{00} mode and m is a large integer given by $m = l_r/\lambda$. For other transverse modes, the longitudinal mode frequencies ω_m may differ depending on the round-trip time t_r for the given transverse mode. Therefore, the density of longitudinal modes increases and, consequently, the spacing between modes decreases with an increase in the number of transverse modes in the cavity, except for a (degenerate) confocal cavity geometry where t_r is the same for all the transverse modes. For a single transverse cavity mode, the longitudinal mode spacing is given by $\Delta\omega_m = 2\pi/t_r$ and equals 0.3 GHz for a 50 cm long cavity. On the other hand, when a large number of transverse modes is excited in the cavity, the longitudinal mode frequencies can overlap and a quasicontinuum of longitudinal cavity modes can result.[7]

The intensity and spectrum of light transmitted through the cavity can be characterized by means of the cavity transmission function. This transmission function is specific for the transverse mode pattern sustained in the cavity and varies with a change of the pulse parameters, such as pulse length, pulse frequency, or pulse linewidth. In specialized cases, this behavior can be conveniently modeled by means of a computer simulation. Here, we present a general analysis of the cavity transmission effects assuming a single transverse cavity mode and approximating the intensity of the signal $S(t+nt_r)$ emerging from the cavity with an expression of the form (see Appendix B)

$$S(t+nt_r) = I_0(\omega)\mathscr{T}(\omega)\exp(-n\mathscr{L}), \tag{7}$$

where $I_0(\omega)$ is the intensity of the single-mode pulse of frequency ω before it enters the cavity, $\mathscr{T}(\omega)$ is the cavity transmission function at ω, and the exponential factor describes the cavity ring-down decay.

The function $I_0(\omega)\mathscr{T}(\omega)$ in Eq. (7) gives the initial intensity of the signal $S(t)$ for a longitudinal mode pulse of frequency ω propagating in the cavity. This initial intensity is measured at some arbitrary time t when the pulse is already completely contained in the cavity, and it may be used to compare cavity transmittivity at different frequencies ω. The explicit form of the function $\mathscr{T}(\omega)$ depends on the relation between the pulse length l_p and the cavity round-trip length l_r. We evaluated $\mathscr{T}(\omega)$ for three separate cases corresponding to a single transverse mode sustained in a cavity with a square pulse of length l_p (a) shorter than l_r, (b) equal to $2l_r$, and (c) longer than the ring-down time τ. We show in Appendix B that

$$\mathscr{T}_a(\omega) = \mathscr{T}^2, \quad l_p < l_r, \tag{8a}$$

$$\mathscr{T}_b(\omega) = 4\mathscr{T}^2\cos^2(\omega t_r/2), \quad l_p = 2l_r, \tag{8b}$$

and

$$\mathscr{T}_c(\omega) = \frac{\mathscr{T}^2}{1-2e^{-1/2\mathscr{L}}\cos\omega t_r + e^{-\mathscr{L}}}, \quad l_p > c\tau. \tag{8c}$$

These three different cases are plotted in Fig. 2 The transmission function $\mathscr{T}(\omega)$ was evaluated for the case of a mechanically stable cavity for which the vibrations of the cavity

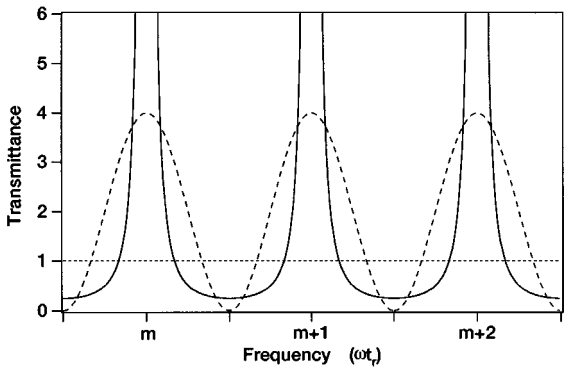

FIG. 2. Transmittance of an optical cavity as a function of pulse frequency for different pulse lengths. The transmittance is given in units equal to the transmittivity of the cavity mirrors $\mathscr{T}^2$. The dotted line represents the transmission function $\mathscr{T}_a(\omega)$ for a pulse l_p whose length is shorter than the cavity round-trip length l_r. The dashed line represents the transmission function $\mathscr{T}_b(\omega)$ for $l_p = 2l_r$. The solid line represents the transmission function $\mathscr{T}_c(\omega)$ for the pulse of the temporal length much longer than the cavity ring-down time τ. The function $\mathscr{T}_c(\omega)$ was calculated assuming a cavity-loss coefficient $\mathscr{L} = 0.01$.

mirrors are of low amplitude and frequency so that its contribution to the broadening of the longitudinal modes of the cavity can be neglected.

For a pulse shorter than l_r, the cavity transmission is not frequency selective and depends only on the mirror transmittivity $\mathscr{T}$ [see Eq. (8a)]. Under these conditions the cavity does not behave as a comblike frequency filter. For a pulse length greater than the round-trip length l_r, the transmission function increases at frequencies resonant with the cavity-mode frequencies and decreases for frequencies off the cavity-mode frequencies. This behavior is common for any pulse of length longer than l_r, regardless of the pulse bandwidth. The spectral modulation of the transmission function $\mathscr{T}(\omega)$ is initially given by a cosine-squared function [see Eq. (8b)], and approaches the ultimate longitudinal mode structure of the optical cavity for pulses of temporal length longer than the ring-down time τ [see Eq. (8c)]. For cosine-squared modulation, the cavity transmission function ranges between $4\mathscr{T}^2$ and 0. For pulses longer than τ, the on-resonance transmittance approaches 100% in the absence of absorption losses, whereas the off-resonance transmittance is proportional to $\mathscr{T}^2/4$.

When the relaxation time T_2 characterizing the absorption line is much shorter than the pulse duration t_p ($T_2 \ll t_p$), the species absorption inside the cavity can be given using the rate approximation (see Appendix A), similar to the case of absorption of cw light. To evaluate absorption under these conditions, the spectrum of light in the cavity must be compared to the absorption linewidth. For the laser pulse longer than l_r, the light inside the cavity persists at the cavity longitudinal modes and the absorption lines that are narrower than the longitudinal mode spacing and lie between the modes cannot absorb the light in the cavity and are not observed in the CRDS spectrum.

A similar limitation holds for the relaxation time T_2 much longer than the pulse duration t_p ($T_2 \gg t_p$), when species in the cavity are absorbing pulsed radiation. These pulses arise from the highly reflective mirrors of the cavity. The relaxation time T_2 is generally a strong function of pressure. For example, under molecular beam conditions it is often expected that $T_2 > t_r$ whereas under atmospheric-pressure conditions it is usually expected that $T_2 < t_r$. When the relaxation time T_2 of the absorbing species is much longer than the round-trip time t_r, each absorber molecule inside the cavity interacts with a sequence of pulses during the time T_2. The molecular polarization induced by this interaction is given approximately by the superposition of polarizations induced by each pulse of the sequence. Consequently, the molecules are polarized and absorb light only at the frequencies that are present in the spectrum of the sequence of pulses. This behavior is the basis of the technique of Ramsey fringes,[15] which was demonstrated as a high-resolution spectroscopic method effective in the optical domain.[16]

For a sequence of identical pulses, the effective spectrum is given by the spectrum of a single pulse times some periodic modulation function that depends on the number of pulses and the pulse spacing. When the pulse sequence is created by the reflections of the laser pulse inside the optical cavity and the pulse matches a single transverse mode of the cavity, this modulation function has the form given by Eq. (8), where $\mathscr{T}_a(\omega)$ is associated with a single pulse, $\mathscr{T}_b(\omega)$ is associated with a sequence of two pulses, and $\mathscr{T}_c(\omega)$ is associated with a train of pulses longer than the ring-down time τ. Consequently, absorber species in the cavity cannot absorb the laser pulse unless the absorption linewidth overlaps the frequency of one or more longitudinal modes of the cavity.

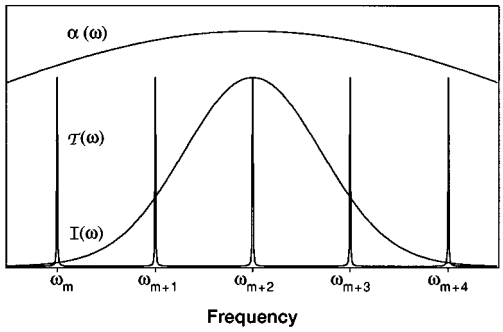

FIG. 3. The line profiles as discussed in Sec. IV. The absorption line $\alpha(\omega)$ is broad compared with the spacing between frequencies ω_m of the cavity longitudinal modes. The laser pulse has a Gaussian profile $I(\omega)$ and length l_p much longer than the cavity round-trip length l_r. Inside the cavity, the pulse oscillates at the longitudinal modes whose frequencies are given by the product of the pulse spectral profile $I(\omega)$ and the cavity transmission function $\mathscr{T}_c(\omega)$ defined in Eq. (8c).

The requirement for the absorption line to overlap the longitudinal modes of the cavity is always met if the absorption linewidth is wider than the spacing between the modes. For the case of $T_2 > t_r$, this condition can be fulfilled only if a sufficient number of transverse modes is sustained in the cavity so that the longitudinal mode spacing is narrower than the absorption linewidth. Such an approach was demonstrated in the work by Meijer *et al.*[7] When only a single transverse mode is sustained in the cavity, the complete absorption spectrum cannot be measured under the condition that $T_2 > t_r$ because the absorption linewidth is narrower than the longitudinal mode spacing and absorption lines can be missed in the CRDS spectrum. To measure a complete absorption spectrum with a single transverse mode in the cavity, the condition of $T_2 < t_r$ must be met by an appropriate adjustment of the cavity length. Under this condition, the spacing between longitudinal modes is always smaller than the absorption linewidth, which guarantees that no absorption lines are missing.

IV. VALIDITY OF THE EXPONENTIAL DECAY MODEL

To investigate the necessary conditions for the exponential decay model to hold, let us consider the experimental situation sketched in Fig. 3. The absorption line is broad compared to the cavity longitudinal mode spacing, and the pulse length is much longer than the cavity round-trip length ($l_p \gg l_r$). The spectral profile of the laser pulse is approximated by a Gaussian function. We consider a resonance conditions, where the line-center frequency of the pulse is tuned to the center of the absorption line, as shown in Fig. 3.

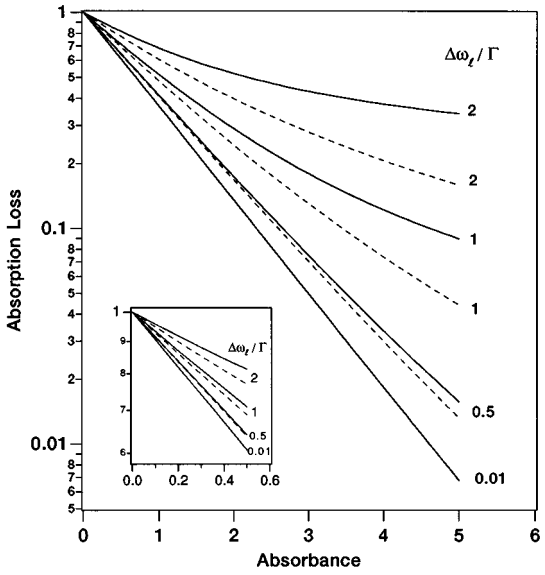

FIG. 4. Plot of the absorption loss [term in braces in Eq. (10)] versus the line-center absorbance for different ratios of the pulse linewidth $\Delta\omega_1$ to the absorption linewidth Γ. The full width of the absorption line $\alpha(\omega)$ is assumed to be ten times the width of the cavity mode spacing. The solid line is the result for the Gaussian profile $\alpha(\omega)$, and the dashed line is the result for the Lorentzian profile $\alpha(\omega)$. The insert shows the approximately linear part of the absorption loss for absorbance less than 0.5

For $l_p \gg l_r$, the light in the cavity persists almost exclusively at the frequencies ω_m of the longitudinal modes after the pulse has filled the cavity. Each mode of frequency ω_m decays exponentially at a rate given by the round-trip loss coefficient $\mathscr{L}(\omega_m)$ of Eq. (6): $\mathscr{L}(\omega_m)=2[(1-R)+\alpha(\omega_m)l_s]$. The ring-down signal S can then be expressed in the form

$$S(t+nt_r)=\sum_m S(t;\omega_m)\exp[-n\mathscr{L}(\omega_m)], \tag{9}$$

where the contributions from different cavity modes are summed to yield the total signal intensity. The number of components in this sum is finite and depends on the number of longitudinal modes that are sustained by the laser pulse in the cavity. When the spacing between the longitudinal modes is small with respect to the absorption linewidth and the pulse linewidth, or the longitudinal modes overlap, the summation over ω_m in Eq. (9) and in the following equations can be replaced by integration.

If the absorption linewidth is comparable to or narrower than the pulse linewidth, the loss coefficient $\mathscr{L}(\omega_m)$ in Eq. (9) varies substantially with frequency ω_m and cannot be factored outside the summation. Under this condition, deviations can be expected from exponential decay. We illustrate this behavior in Fig. 4, where the line-center sample absorption loss is plotted as a function of the dimensionless absorbance (line-center absorption coefficient times the total pathlength of the pulse in the sample) for different ratios between the pulse linewidth $\Delta\omega_1$(FWHM) and absorption linewidth Γ (FWHM). The loss caused by the sample absorption was determined by transforming Eq. (9) with the help of Eq. (6) into the form

$$S(t+nt_r)=S(t)\exp[-2n(1-\mathscr{R})] \times\left\{\frac{1}{S(t)}\sum_m S(t;\omega_m)\exp[-2n\alpha(\omega_m)l_s]\right\}, \tag{10}$$

where

$$S(t)=\sum_m S(t;\omega_m). \tag{11}$$

The loss caused by the sample absorption is represented by the term in braces in Eq. (10).

The deviation from exponential ring-down decay becomes significant for long observations times, which are associated with the pulse absorption pathlengths equal to several line-center absorption lengths α^{-1}. For the absorption pathlength shorter than α^{-1}, the decay remains approximately exponential, even if the pulse linewidth is wider than the absorption linewidth (see the insert in Fig. 4).

In practice, the length of the observation time is limited by the dynamic range of the detection system used to acquire and digitize the ring-down waveform. It is justified, therefore, to restrict the observation time to about 5τ, where τ is the ring-down time for the system.[17] During the observation time 5τ, the signal intensity decreases by about 99%. For sample absorption loss constituting about 10% of the total cavity loss, the observation time 5τ is associated with an absorbance value of 0.5.

If sample absorption is the major source of the cavity loss, the pulse travels a few absorption lengths α^{-1} during the observation time and the absorbance is greater than one, giving nonexponential ring-down for wide pulse linewidths. Conversely, for weak sample absorption compared to the cavity loss, the absorbance is less than one and the decay of the pulse is nearly exponential. This behavior is reflected in Eq. (10) where, for small absorbances ($2n\alpha l_s \ll 1$), the exponential term $\exp[-2n\alpha(\omega_m)l_s]$ can be replaced by the leading two terms in its power series expansion $1-2n\alpha(\omega_m)l_s$. Equation 10 then reduces to

$$S(t+nt_r)=S(t)(1-2n\alpha_{\text{eff}}l_s)\exp[-2n(1-\mathscr{R})], \tag{12}$$

where

$$\alpha_{\text{eff}}=\frac{\sum_m S(t;\omega_m)\alpha(\omega_m)}{S(t)} \tag{13}$$

is the effective absorption coefficient. Under the condition that $2n\alpha l_s \ll 1$, the term $2n\alpha_{\text{eff}}l_s$ in Eq. (12) is much smaller than the unity, and $1-2n\alpha_{\text{eff}}l_s \cong \exp(-2n\alpha_{\text{eff}}l_s)$. Consequently, the signal $S(t+nt_r)$ decreases approximately exponentially in time

$$S(t+nt_r)=S(t)\exp\{-2n[(1-\mathscr{R})+\alpha_{\text{eff}}l_s]\}. \tag{14}$$

Based on the work of Crisp,[13] we conclude that for small absorbance values a similar, approximately exponential behavior can be observed for the pulse whose linewidth arising from the pulse shortness is wider than the absorption linewidth.

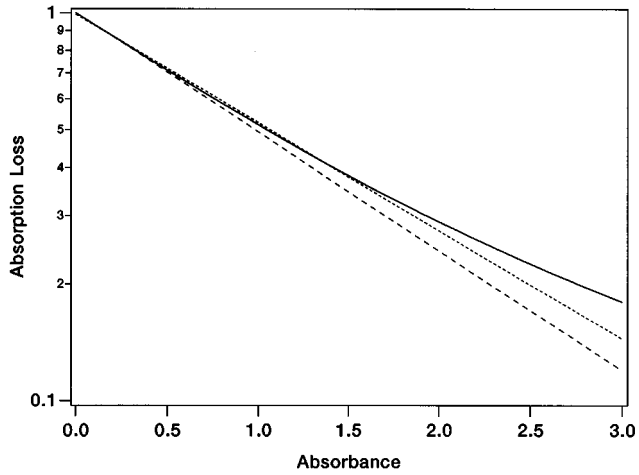

FIG. 5. Plot of absorption loss versus absorbance. The solid line is the plot for the observed ring-down decay [Eq. (10)]; the dotted line is the plot for the ring-down decay assuming exponential behavior [Eq. (10) fit to Eq. (14)], and the dashed line, for the ring-down decay approximated by an effective absorption coefficient α_{eff} [Eq. (14)]. The absorption line is assumed to have a Gaussian profile whose width Γ equals the pulse width $\Delta\omega_1$. The fit of Eq. (10) to Eq. (14) was obtained with the standard fitting procedure, by taking the natural logarithm of the wave form given by Eq. (10) [$\ln(y)$] and fitting it to the natural logarithm of Eq. (14) with (y^2) weighting.

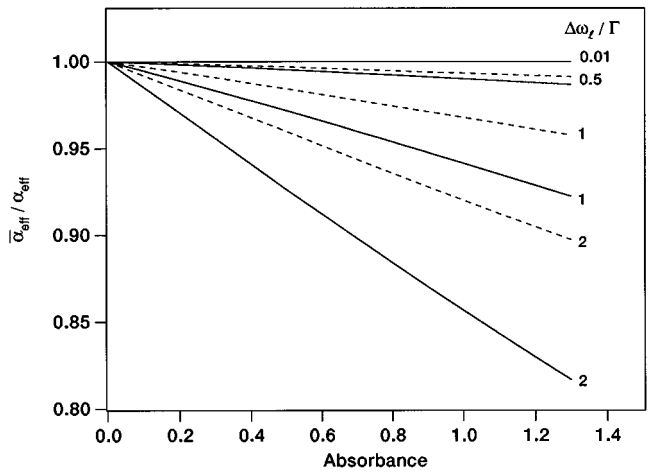

FIG. 6. Plot of the ratio of the effective absorption coefficient α_{eff} given by Eq. (13) to the estimate of the fit value $\bar{\alpha}_{\text{eff}}$, as a function of the absorbance for different values of $\Delta\omega_1/\Gamma$, where $\Delta\omega_1$ is the laser pulse linewidth and Γ is the absorption linewidth. This ratio estimates the accuracy in α_{eff} determination from the fit of the approximately exponential ring-down wave form to Eq. (14). This accuracy is less for wider pulse linewidths and decreases with the increase in the absorption pathlength. The fit value $\bar{\alpha}_{\text{eff}}$ was estimated by taking the natural logarithm of the absorption loss given by the term in braces in Eq. (10) and dividing it by the absorption pathlength.

The effective absorption coefficient α_{eff} can be deduced from the slope of a plot of the absorption loss versus time in the insert to Fig. 4. The amplitude of α_{eff} changes with the pulse linewidth, approaching the actual value of the absorption coefficient α in the limit of narrow linewidth and decreasing with an increase in the linewidth. Despite these changes in the amplitude, the effective absorption coefficient α_{eff} can be used as a measure of the relative absorption of the gas sample provided that the absorption lines are of the same, constant width. From such a measurement the relative concentration or temperature of the sample can be obtained. Because the value of α_{eff} decreases with an increase in the pulse linewidth, these measurements will decrease in sensitivity, as the pulse linewidth exceeds the absorption linewidth.

In what follows we parametrize these deviations from Beer's law behavior in terms of dimensionless plots. We assume that the observed ring-down decay waveform is described by Eq. (10). The effective absorption coefficient $\bar{\alpha}_{\text{eff}}$ is obtained by fitting the observed decay waveform, given by Eq. (10), to Eq. (14). The absorption loss predicted by Eq. (10), the absorption loss approximated by Eq. (14), and the result of the fit are plotted in Fig. 5 as a function of the absorbance, for the Gaussian absorption line of FWHM Γ equal to the linewidth $\Delta\omega_1$ of the laser pulse. The value of the coefficient $\bar{\alpha}_{\text{eff}}$ resulting from the fit varies depending on the way the experimental points are weighted within the fit procedure, and is smaller than the value of the coefficient α_{eff} predicted by Eq. (13). Only under the condition where the decay is exactly exponential does the coefficient $\bar{\alpha}_{\text{eff}}$ from the fit equal the coefficient α_{eff} given by Eq. (13).

The accuracy of the determination of the effective absorption coefficient α_{eff} can be evaluated with the help of Fig. 6, where the ratio of the effective absorption coefficient α_{eff} given by Eq. (13) to the estimate of the fit value $\bar{\alpha}_{\text{eff}}$ is plotted as a function of the absorbance. The most accurate value of α_{eff} can be measured for small absorbances, as expected. Nevertheless, for an absorbance equal to 0.5 and the pulse linewidth twice as wide as the absorption linewidth, $\bar{\alpha}_{\text{eff}}$ differs from α_{eff} by less than 10%.

In place of the line center absorption coefficient, the integrated absorption coefficient $\int \alpha(\omega) d\omega$ is frequently used as a measure of absolute absorption. This quantity does not suffer from line broadening effects. The integrated coefficient can be directly obtained from the integration of the effective coefficient $\alpha_{\text{eff}}(\omega_{\text{lc}})$ as a function of the line-center frequency ω_{lc} of the laser pulse. The coefficient $\alpha_{\text{eff}}(\omega_{\text{lc}})$ depends on laser frequency ω_{lc} through the intensity factors $S(t;\omega_m)$ and $S(t)$. When the laser line covers a number of frequencies ω_m sufficient to replace the summation over m by integration, the factor $S(t)$ does not depend on the laser frequency ω_{lc} and equals the integral of $S(t;\omega_m)$ over ω_{lc}. This relation holds for any longitudinal mode ω_m over which the laser frequency is scanned. Therefore, by integration of both sides of Eq. (13) over the frequency ω_{lc} we obtain

$$\int \alpha_{\text{eff}}(\omega_{\text{lc}}) d\omega_{\text{lc}} = \sum_m \alpha(\omega_m) \Delta\omega_m , \tag{15}$$

where $\Delta\omega_m$ is the spacing between the cavity longitudinal modes.

When the absorption line is wide enough to replace the summation over m by integration, Eq. (15) can be used to determine the integrated absorption coefficient from the measurement of the effective coefficient α_{eff} as a function of laser frequency. We estimate that for a laser pulse having a Gaussian profile whose FWHM is wider than $\Delta\omega_m$ the factor $S(t)$ differs from the ω_{lc} integral of $S(t;\omega_m)$ by no more than

TABLE I. Limiting cases of CRDS.

Limiting cases	Appearance of light absorbed by sample	Appearance of modes	Absorption linewidths vs maximum possible mode spacing[a]
1[b] $t_p \gg T_2 \gg t_r$	cw	Yes	Narrower
2[b] $t_p \gg t_r \gg T_2$	cw	Yes	Wider
3 $t_r \gg t_p \gg T_2$	cw	No	Wider
4[b] $T_2 \gg t_p \gg t_r$	Pulsed	Yes	Narrower
5 $T_2 \gg t_r \gg t_p$	Pulsed	Yes	Narrower
6 $t_r \gg T_2 \gg t_p$	Pulsed	No	Wider

[a]Maximum possible mode spacing is given by $\Delta\omega_m = l_r^{-1}$ (cm^{-1}), independent of whether modes actually develop.
[b]Pulse duration t_p greatly exceeds round-trip time t_r.

$\pm 10\%$. Furthermore, for a Gaussian or Lorentzian absorption line profile with a FWHM wider than the spacing $\Delta\omega_m$ between the cavity modes, the relation (15) approximates the integrated absorption coefficient to within 10%.

V. CONCLUSION

Two requirements must be met for CRDS to be a useful diagnostic tool: (1) as the pulsed light source is tuned in frequency, the CRDS spectrum is obtained with sufficient resolution so that the full absorption spectrum can be recovered without missing absorption features; and (2) the ring-down waveform decays exponentially so that the CRDS signal can be directly related to the absorption spectrum of the sample without a knowledge of the pulse characteristics. The first requirement arises because the light absorbed by the species inside the cavity can consist of longitudinal modes whose spacing is defined by the cavity geometry and the number of transverse modes inside the cavity. When the species are absorbing under the rate approximation regime ($T_2 \ll t_p$), these modes can be associated with cavity etalon effects, whereas for the species absorbing pulses of light in a coherent regime ($T_2 \gg t_p$), the modes are so-called Ramsey fringes. Therefore, the analysis of requirement (1) is complicated because of the need to consider three different time scales, the pulse duration, t_p, the round-trip time of the pulse inside the optical cavity, t_r, and the relaxation time of the absorber T_2. Table I presents six limiting cases, which were discussed in more detail in Sec. III. We conclude, that for the measurement of the smooth, complete absorption spectrum by CRDS the absorption linewidth must be wider than the spacing between the cavity longitudinal modes. For cases 2, 3, and 6 this requirement is always fulfilled because the absorption linewidth is broader than the maximum possible longitudinal mode spacing $\Delta\omega_m = l_r^{-1}$, even though modes do not appear in cases 3 and 6. When the FWHM absorption linewidth Γ is narrower than $\Delta\omega_m = l_r^{-1}$ (cases 1, 4, and 5), the CRDS spectrum can be still measured providing that a sufficient number of transverse modes is sustained in the cavity so that the resulting spacing between the longitudinal modes is smaller than Γ.

The second requirement for CRDS to be applicable as a quantitative disgnostic is to fulfill the conditions for exponential ring-down decay. The exponential model of the ring-down decay, which predicts that the inverse of the ring-down time varies linearly with the absorption coefficient, is strictly valid only if the absorption linewidth is much broader than the linewidth of light circulating in the cavity. Because the linewidth of light in a cavity is controlled by the linewidth of the laser pulse injected into the cavity, CRDS measurements gain in accuracy as the pulse linewidth decreases with an increase of both the pulse coherence length and spatial length. Although this implies that the ultimate accuracy of CRDS measurements can be achieved using a monochromatic, cw laser beam that is tuned into resonance with consecutive cavity longitudinal modes as the laser frequency is scalled across the absorption line, the CRDS technique can still be used accurately by choosing the laser pulse to have a width that spans the longitudinal cavity modes.

When the absorption linewidth is comparable to the linewidth of light circulating in the cavity, CRDS can provide a useful absorption spectrum provided that the absorption loss constitutes a small fraction of the total cavity loss. Figure 4 presents a dimensionless plot describing how the absorption loss varies with the absorbance of the sample for various ratios of the laser pulse linewidth to the absorption linewidth for either a Gaussian or a Lorentzian absorption line shape. For absorbances $2n\alpha(\omega)l_s$ less than unity, the absorption loss increases exponentially with the absorbance, and an effective absorption coefficient α_{eff} can be readily defined under this condition. The effective coefficient α_{eff} is proportional to the inverse of the decay time τ but changes with the width of the absorption line and is smaller than the actual value of the absorption coefficient α. Integration of the effective coefficient α_{eff} over wavelength, however, gives to high accuracy the value of the integrated absorption coefficient. This integration permits the determination of the absolute absorption coefficient from a CRDS spectrum in a way that is insensitive to the changes in both the absorption linewidth and pulse linewidth.

These considerations allow CRDS to become a practical, quantitative diagnostic method for species that can be placed inside a highly reflective optical cavity. A wide range of conditions exist and can be met in which the ring-down waveform can be clearly approximated as exponential and the full absorption spectrum can be recovered from a recording of the ring-down decay time versus frequency.

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APPENDIX A: BEER'S LAW BEHAVIOR

Our treatment closely follows that of Meystre and Sargent.[12] To describe absorption of the molecular sample in an optical cavity, consider a pulse interacting with a molecular system in which g and e denote the ground and excited state. Diagonal elements $\rho_{gg}(z,t)$ and $\rho_{ee}(z,t)$ of a two-level density matrix are populations of the ground and excited

levels, and nondiagonal elements $\rho_{eg}(z,t)[\rho_{ge}(z,t)]$ contribute to the macroscopic dipole polarization $\mathbf{P}(z,t)$ of the absorbing medium in the cavity

$$\mathbf{P}(z,t)=\mathrm{Tr}(\mu^{\dagger}\rho(z,t))\equiv\mu_{eg}\rho_{ge}+\mathrm{cc}, \tag{A1}$$

where μ is the dipole moment operator for the molecule. Polarization $\mathbf{P}(z,t)$ is a source term in the wave equation that will be used to describe the propagation of the pulse.

A pulse propagates in a cavity along the z axis. Typically, it is 5–15 ns in duration and consists of a single longitudinal mode or of a number of closely spaced single modes forming a multimode structure. For linear absorption, these modes are not coupled and propagate independently. Therefore, absorption of each of the modes will be considered separately; the overall pulse absorption is calculated by summation of the single-mode contributions.

For a molecule interacting with a longitudinal mode of frequency ω_i, the interaction operator in the rotating wave approximation takes the form

$$\mathscr{V}_{eg}(z,t)=-(1/2)\mu_{eg}\mathscr{E}_i(z,t)e^{i(k_iz-\omega_it)}. \tag{A2}$$

The density matrix element ρ_{eg} induced by the interaction (A2) evolves according to the Liouville equation, which after formal integration gives

$$\rho_{eg}(z,t)=\frac{i}{\hbar}\int_{-\infty}^{t}dt'\ e^{-(\gamma+i(\omega_{eg}-k_iv}(t-t')\times\mathscr{V}_{eg}(z,t')[\rho_{ee}(z,t')-\rho_{gg}(z,t')]. \tag{A3}$$

Here, $h\omega_{eg}$ is the energy gap between excited and ground level, and k_iv describes the Doppler shift for molecules moving with velocity v along the z axis.

For many media, including gas cells and molecular beams (in a direction perpendicular to the beam axis), the velocity v has a Maxwell–Boltzmann distribution

$$W(v)=\frac{1}{\sqrt{\pi}\Delta v}\exp\left[-\left(\frac{v}{\Delta v}\right)^2\right];\quad \Delta v=\left(\frac{2kT}{m}\right)^{1/2}. \tag{A4}$$

By averaging Eq. (A3) over the velocity distribution (A4) we obtain

$$\rho_{eg}(z,t)=\frac{i}{\hbar}\int_{-\infty}^{t}dt'\ \exp-(\gamma(t-t')+(k_i\Delta v/2)^2(t-t)^2+i\omega_{eg}(t-t'))\times\mathscr{V}_{eg}(z,t')[\rho_{ee}(z,t')-\rho_{gg}(z,t')]. \tag{A5}$$

The exponential in Eq. (A5) includes two terms that control the rate of decay of the dipole: the homogeneous width γ and the Doppler width Δv. The decay time T_2 can be found as a solution of the quadratic equation

$$\gamma T_2+(k_i\Delta v/2)^2(T_2)^2=1, \tag{A6}$$

whose solution is $T_2=1/\gamma$ for purely homogeneous broadening and $T_2=2/k_i\Delta v$ for purely inhomogeneous, Doppler broadening. When the decay time T_2 is much shorter than the time in which the pulse envelope $\mathscr{E}_i(z,t)$ or populations ρ_{ee} and ρ_{gg} can change, Eq. (A5) can be integrated over dt' such that both $\mathscr{E}_i(z,t)$ and the population terms can be moved outside the integral

$$\rho_{eg}(z,t)=-\frac{i}{2\hbar}N\mu_{eg}\mathscr{E}_i(z)e^{i(k_iz-\omega_it)}\times\int_{-\infty}^{+\infty}dv\ W(v)\ \frac{1}{\gamma+i(\omega_{eg}-k_iv-\omega_i)}. \tag{A7}$$

which allows us to formulate Beer's law for absorption.

The approximation of a slowly varying population is well fulfilled for the system because the intensity of light in a cavity is weaker than the saturation intensity and, consequently, the population is not altered by interaction with the pulse. The population difference N is equal to the value $N=\rho_{ee}(z,-\infty)-\rho_{gg}(z,-\infty)$.

The approximation of a slowly varying field envelope introduces constraints for the maximum variation of the intensity of light in a cavity and thereby limits the minimum length of the pulse. This restriction resembles the observation by Crisp[13] that the absorption of a coherent pulse can be described by Beer's law only for a pulse length long with respect to the time T_2.

The macroscopic polarization $\mathbf{P}(z,t)$ for the wave ω_i can be found by combining expressions (A1) and (A7). This polarization constitutes a generic term in the Maxwell equation of motion. Under the slowly varying envelope approximation, we have

$$\frac{d\mathscr{E}_i(z)}{dz}\ e^{i(\mathbf{k}_i\mathbf{z}-\omega_i\mathbf{t})}=-\alpha(\omega_i)\mathscr{E}_i(z)e^{i(\mathbf{k}_i\mathbf{z}-\omega_i\mathbf{t})}, \tag{A8}$$

where a complex coefficient of absorption $\alpha(\omega)$ is expressed in the usual form

$$\alpha(\omega)=-\frac{k\mu_{eg}^2}{2\epsilon\hbar}N\int_{-\infty}^{+\infty}dv\ W(v)\times\left(\frac{\gamma}{\gamma^2+(\omega_{eg}-kv-\omega)^2}-i\frac{(\omega_{eg}-kv-\omega)}{\gamma^2+(\omega_{eg}-kv-\omega)^2}\right). \tag{A9}$$

The real part of the coefficient $\alpha(\omega)$ describes absorption and the imaginary part of $\alpha(\omega)$ describes dispersion. As a result of dispersion, the pulse velocity in the absorbing medium changes as a function of detuning from resonance. This dispersion effect can influence the ring-down time τ through the change in the round-trip time t_r. We estimate, however, that the maximum change in the ring-down time τ that is caused by the dispersion is on the order of the optical period $1/\omega$, i.e.,

$$|\Delta\tau|<\frac{1}{\omega}\left|\frac{\mathrm{Im}(\alpha)}{\mathrm{Re}(\alpha)}\right|\leqslant\frac{1}{\omega}\frac{|\omega_{eg}-\omega|}{\gamma}. \tag{A10}$$

Consequently, dispersion effects are negligible.

Equation (A8) can be transformed into Beer's law for absorption of a wave of frequency ω_i:

$$\frac{dI(z)}{dz}=-2\ \mathrm{Re}[\alpha(\omega_i)]I(z). \tag{A11}$$

In a cavity, there are two counterpropagating waves at frequency ω_i. For linear absorption, however, the forward $(+k)$ and backward $(-k)$ propagating waves can be considered independently, and the equations will have the same form for both directions of propagation because of the symmetry of distribution $W(v)$. Therefore, by integrating Eq. (A11) over the round-trip path, starting, for example, from the exit mirror of the cavity, and then summing over frequencies ω_i, we obtain the round-trip pulse absorption. Because of the resonant character of absorption, that sum includes different values of absorption coefficients for waves of different frequency ω_i. Expressing a round-trip absorption with a single absorption coefficient α requires the absorption feature to be wider than the bandwidth of frequencies ω_i so that $\alpha(\omega_i)$ can be replaced by an average value. Under these conditions, $\alpha(\omega_i)$ can be taken outside the ω_i summation as a quantity that varies only with the laser line-center frequency $\omega_{\rm lc}$. This factorization yields Beer's law for the pulse absorption inside the cavity.

APPENDIX B: FABRY–PEROT THEORY

Consider a single-mode laser pulse that has an initial amplitude

$$E_0(z,t)=(1/2)\mathscr{E}_0(z,t)e^{i(kz-\omega t)}+\text{cc}, \tag{B1}$$

which is injected into an optical cavity. The pulse forms a single transverse mode of the cavity, for which the amplitude of the field at the transmitting mirror can be expressed in the form

$$E(t+nt_r)=\tfrac{1}{2}\sqrt{\mathscr{T}}\exp[-n(\tfrac{1}{2}\mathscr{L}+i\omega t_r)] \times\sum_r\ [\exp(-r\mathscr{L})]^{1/2}\mathscr{E}_0(rl_r,t)e^{ir\omega t_r}+\text{cc}. \tag{B2}$$

In Eq. (B2), $\sqrt{\mathscr{T}}$ describes a transmittance of the cavity entrance mirror, the summation over r accounts for the overlap of pulse fragments in the cavity and gives the initial amplitude $E(t)$ of the light inside the cavity, and the exponential term in front of the summation represents the ring-down decay. The number of components in the summation over r is finite and depends on the ratio between the pulse length and the round-trip length l_r. The light intensity corresponding to the amplitude (B2) is given by

$$I(t+nt_r)=\mathscr{T}\exp(-n\mathscr{L})\langle\mathscr{E}_0[\mathscr{E}_0]^*\rangle \times\left|\sum_r\ [\exp(-r\mathscr{L})]^{1/2}e^{ir\omega t_r}\right|^2, \tag{B3}$$

where for the square pulse the field amplitude $\mathscr{E}_0(z,t)$ is replaced with constant amplitude $\mathscr{E}_0$.

In Eq. (B3), the intensity $I(t+nt_r)$ is given as a product of the pulse initial intensity $I_0=\langle\mathscr{E}_0[\mathscr{E}_0]^*\rangle$ and the frequency-dependent interference factor that defines the spectral characteristics of the cavity transmission function $\mathscr{T}(\omega)$. The output signal $S(t+nt_r)$ can be expressed in the form

$$S(t+nt_r)=I_0(\omega)\mathscr{T}(\omega)\exp(-n\mathscr{L}), \tag{B4}$$

where

$$\mathscr{T}(\omega)=\mathscr{T}^2\left|\sum_r\ [\exp(-r\mathscr{L})]^{1/2}e^{ir\omega t_r}\right|^2 \tag{B5}$$

is the cavity transmission function. Equation (8) is derived from Eq. (B4) by using for the function $\mathscr{T}(\omega)$ the explicit form for the case of (a) $r=0$, (b) $r=0$, 1, and (c) $r=0$, 1,..., n as n goes to infinity.

[1] A. O'Keefe and D. A. G. Deacon, Rev. Sci. Instrum. **59**, 2544 (1988).
[2] D. Romanini and K. K. Lehmann, J. Chem. Phys. **99**, 6287 (1993).
[3] D. Romanini and K. K. Lehmann, J. Chem. Phys. (to be published, 1995).
[4] A. O'Keefe, J. J. Scherer, A. L. Cooksy, R. Sheeks, J. Heath, and R. J. Saykally, Chem. Phys. Lett. **172**, 214 (1990).
[5] T. Yu and M. C. Lin, J. Am. Chem. Soc. **115**, 4371 (1993).
[6] T. Yu and M. C. Lin, J. Phys. Chem. **98**, 9697 (1994).
[7] G. Meijer, M. G. H. Boogaarts, R. T. Jongma, D. H. Parker, and A. M. Wodtke, Chem. Phys. Lett. **217**, 112 (1994).
[8] D. J. Bernard and B. K. Winker, J. Appl. Phys. **69**, 2805 (1991).
[9] R. T. Jongma, M. G. H. Boogaarts, and G. Meijer, J. Mol. Spectrosc. **165**, 303 (1994).
[10] P. Zalicki, Y. Ma, R. N. Zare, J. R. Dadamio, E. H. Wahl, T. G. Owano, and C. H. Kruger, *47th Annual Gaseous Electronics Conference*, Gaithersburg, Maryland, 1994.
[11] M. Billardon, M. E. Couprie, J. M. Ortega, and M. Velghe, Appl. Opt. **30**, 344 (1991).
[12] P. Meystre and M. Sargent III, *Elements of Quantum Optics*, 2nd ed. (Springer, Berlin, 1991).
[13] M. D. Crisp, Phys. Rev. A **1**, 1604 (1970).
[14] D. Z. Anderson, J. C. Frisch, and C. S. Masser, Appl. Opt. **23**, 1238 (1984).
[15] W. Demtröder, *Laser Spectroscopy* (Springer, Berlin, 1988).
[16] T. W. Hänsch, in *Laser Spectroscopy III*, Proceedings of 3rd Intern. Conf., Jackson Lake, 1977, edited by J. L. Hall and J. L. Carlsten (Springer, Berlin, 1977), p. 149.
[17] The detection system may show deviations from exponential decay for early recording times because of the response to transients. Therefore, in practical work the early-time part of the CRDS wave form may need to be omitted.