Infrared cavity ringdown laser absorption spectroscopy (IR-CRLAS)

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Abstract

We report the first extension of cavity ringdown laser absorption spectroscopy (CRLAS) into the infrared region. Spectra of static gas samples have been obtained employing a single mode Nd:YAG pumped optical parametric oscillator laser system and are reported for two spectral regions centered around 1.6 and 3.3 μm, respectively. We also explore the issue of the frequency specificity of the ringdown cavity. Specifically, we demonstrate the ability to extract accurate absorption intensities when the width of the spectral feature is much smaller than the free spectral range of the cavity, in direct contrast to recently published theoretical predictions.

1. Introduction

Gas phase spectroscopic techniques have served as a powerful tool for a wide range of disciplines in chemistry and physics, including cluster research, atmospheric chemistry, and combustion diagnostics. The ability to accurately determine relative absorption intensities, cross sections, and species concentrations is fundamental to the above areas of research, and numerous techniques have been employed to this end. Established techniques for visible–UV studies include laser induced fluorescence (LIF), resonant ionization methods (REMPI), intracavity absorption spectroscopy, four-wave mixing (e.g. DFWM), conventional absorption methods, photoacoustic spectroscopy (PA), and cavity ringdown absorption spectroscopy (CRLAS). However, only the absorption based techniques such as CRLAS, are generally applicable for studies which aim to determine absolute species concentrations or cross sections.

Spectroscopic techniques currently employed for infrared work include cw-based methods such as diode laser spectroscopy and resonant photoacoustic spectroscopy, and pulsed methods such as DFWM and CARS. Although demonstrated to be highly sensitive, cw based methods are not ideally suited for the study of trace species in transient environments, since the associated duty cycles can degrade perfor-
mance by orders of magnitude (see e.g. Ref. [1]). Additionally, the ability to cover large spectral regions is severely limited by the slow scanning speeds and limited operating ranges of laser systems such as diode lasers and F-center lasers. Recently, pulsed methods such as degenerate four wave mixing (DFWM) have been demonstrated with the use of high power, tunable pulsed infrared laser sources [2]. Although extremely sensitive for applications in low pressure environments, DFWM experiments can be severely limited at elevated pressures, where the ability to establish gratings is severely impaired by the dephasing effects of collisions. Additionally, complex models are frequently required to deconvolute the experimentally observed spectral intensities (see e.g. Ref. [3]). The above points underscore the need for an infrared direct absorption method which possesses generality, high sensitivity, rapid scanning ability, and wide wavelength coverage. In these respects, CRLAS would prove invaluable for infrared studies.

In this Letter, we report the first extension of the cavity ringdown technique into the infrared, and demonstrate the generality and high sensitivity of the technique for infrared spectroscopic studies. This extension is largely due to a combination of new optical coating capabilities with recently available tunable pulsed laser sources. The ability to obtain accurate absorption intensities is demonstrated in two spectral regions under Doppler limited conditions in (room temperature) static gas cells, with comparisons to data obtained with other methods. In the 1.6 μm region, overtone spectra of acetylene are presented and directly compared with the recently reported photoacoustic spectra of Hornberger et al. [4]. In the 3.3 μm region, data for methane are presented and compared to those obtained with difference frequency absorption spectroscopy [5]. Additionally, the single mode properties of the laser system have facilitated experiments which investigate the role of longitudinal mode effects in the transient ringdown cavity. In particular, we show that ringdown spectroscopy produces reliable absorption intensities in cases where the bandwidth of the injection laser and the linewidth of the absorber are narrower than the free spectral range (longitudinal mode spacing) of the resonator, in direct contrast to the recently reported theoretical conclusions of Zaliiki and Zare [6].

2. Cavity ringdown laser absorption spectroscopy (CRLAS)

In the pulsed cavity ringdown technique, initially developed by O'Keefe and Deacon [7], the transmissivity of an optical cavity is determined from the measured photon decay time, or 'ringdown' time of the resonator. The method is based on measurement of the time rate of decay of a pulse of light trapped in a high finesse optical cavity. A pictorial representation in the short pulse limit is presented in Fig. 1. Pulsed laser light is injected into a cavity formed by a pair of highly reflective (typically \( R > 99.9\% \)) mirrors. 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. Instead, the light pulse acts like a ‘particle’ as it circulates in the cavity. A detector placed after the exit mirror records a series of pulses, spaced by the transit time of the

![Fig. 1. Schematic of the CRLAS method. Pulsed laser light is injected into an optical resonator formed by a pair of highly reflective mirrors (\( R > 99\% \)). The intensity of the trapped light is monitored via transmission through the exit mirror of the resonator as a function of time, allowing the cavity decay or ‘ringdown’ time to be determined. Theoretical sensitivity limits of the method are dictated by the mirror reflectivities and the precision of the decay time measurement.](image-url)
cavity. For each round trip, the trapped light intensity diminishes proportionally to the transmission factor $T$ of the cavity, according to

$$\frac{dl}{dt} = -\frac{TcL}{2L},$$

where $L$ is the mirror spacing and $c$ is the speed of light. The solution of Eq. (1) is given by

$$I = I_0 e^{-TcL/2L},$$

which states that the intensity envelope of these pulses exhibits a simple exponential decay. The time required for the resonator to decay to $1/e$ of the initial output pulse is called the 'cavity ringdown' time. Ideally, the ringdown time is a function of only the mirror reflectivities, cavity dimensions, and the sample absorption (for samples placed between the mirrors). Absolute absorption intensities are determined by subtracting the baseline transmission of the cavity, which is determined when the laser wavelength is off resonance with all molecular transitions. Every laser pulse constitutes an independent measurement, hence the method is not seriously degraded by the large pulse to pulse intensity fluctuations common to pulsed laser systems.

The high sensitivity of the method for spectroscopic applications was first demonstrated by O'Keefe et al. by measuring doubly forbidden electronic transitions in molecular oxygen. In CRLAS, sensitivity is determined by the mirror reflectivities and the precision of the decay time measurement [8]. The high sensitivity of the method stems from the relaxed constraints on the accuracy of the time constant measurement, which only need be determined to $\approx 1\%$ (for typical highly reflective cavities) in order to determine a fractional absorption of a few parts per million (see e.g. Ref. [9]). Sensitivity limits for various cavity configurations are discussed in detail in Ref. [8].

Since, the initial work of O'Keefe et al., on static gas cells, CRLAS has been extended to molecular beam spectroscopy [10–12], kinetics studies [13,14], microwave discharges [15], and the spectroscopy of flames [16]. All reported studies to date were conducted in the visible and UV regions of the spectrum. In this Letter, we present the first extension of the technique into the infrared.

### 3. Experimental apparatus

A diagram of the experimental apparatus is shown in Fig. 2. The probe laser system consists of an injection seeded pulsed Nd:YAG laser (Spectra

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**Fig. 2.** The Sandia IR-CRLAS apparatus: single mode pulsed infrared laser light is generated in an optical parametric oscillator (OPO) and coupled into the ringdown cavity cell with a simple telescope. The transmitted light is detected with either a fast InGaAs photodiode or a nitrogen-cooled InSb detector, amplified, digitized, and transferred to a computer for analysis. The absorption intensities are obtained by determining the total cavity losses (per pass) at different frequencies, and subtracting the baseline losses of the cavity.
Simple static gas cells were constructed to demonstrate the generality of the method in this new spectral region and to facilitate a comparison with data obtained with other methods. In both spectral regions, the data are obtained under Doppler-limited conditions, leading to spectral widths on the order of 0.02 and 0.01 cm\(^{-1}\), respectively, for the 1.6 and 3.3 \(\mu\)m regions. The cell is evacuated with either a small turbo pump or a roughing pump, and the absolute pressure of the gas is monitored with a Baratron (MKS 390HA). In the 1.6 \(\mu\)m region, mirror reflectivities are measured to be \(\approx 99.99\%\), with an experimentally realized sensitivity of \(2 \times 10^{-6}\), while the 3.3 \(\mu\)m mirrors were found to be only 99.2% reflective with a markedly lower associated sensitivity of \(4 \times 10^{-4}\). These sensitivities are roughly an order of magnitude from the theoretical limit, in the current configuration (see e.g. Ref. [8]). It is anticipated that improvements in mirror coatings \((R > 99.95\%)\) in the 3.3 \(\mu\)m region will improve the technique sensitivity by nearly two orders of magnitude.

4. Results

In this section, IR-CRLAS data are presented for two regions in the infrared, centered around 1.6 and 3.3 \(\mu\)m, respectively. In the 1.6 \(\mu\)m region, overtone spectra of acetylene are presented and compared with recently reported data acquired with resonant photoacoustic spectroscopy (PAS). IR-CRLAS spectra obtained at different cell pressures demonstrate at least an order of magnitude greater sensitivity than the PAS work. In the 3.3 \(\mu\)m region, the Q-branch features of the \(v_3\) fundamental band of methane are recorded at low concentration and are compared to data obtained with difference frequency absorption spectroscopy.

4.1. 1.6 \(\mu\)m region

IR-CRLAS spectra of the weak overtone spectra of acetylene at 6460 cm\(^{-1}\) are shown in Fig. 3, and include assignments for P-branch transitions from several previously reported vibrational combination bands [17]. In this scan, 830 mTorr of \(C_2H_2\) (99% purity) filling a cell 39 cm long is probed at 0.0025 cm\(^{-1}\) intervals with an average of 16 laser shots per
wavelength point. The experimentally determined sensitivity in this scan is typically 3–4 ppm, with a best value of 2 ppm obtained in these studies. This high sensitivity is due to the highly reflective mirrors ($R = 99.99\%$) used in this spectral region.

Comparison of the IR-CRLAS data with the recently published photoacoustic data of Hornberger et al. [4] allows a direct comparison of the sensitivity of the two techniques. In the photoacoustic experiment, Doppler-limited spectra were obtained with a single mode F-center laser and a radially resonant photoacoustic cell 45 cm in length, and an acetylene cell pressure of $\approx 12.5$ Torr. The radially resonant design incorporated in that work significantly increases sensitivity over conventional photoacoustic methods. The spectral region shown in Fig. 3 was tailored to match that presented in the PAS work, to facilitate comparison. Comparison of the IR-CRLAS data with the PAS data indicates extremely similar relative intensities for the various spectral lines, with the exception of the stronger features such as the P(26) 10110–00010 rovibrational transition, which are weaker in the PAS work. IR-CRLAS data were also recorded at cell pressures of 4.5 Torr, 1.7 Torr, and 40 mTorr, to check for the proper Beer's law behavior in our absorption data, and were found to consistently produce the same relative intensities. From these results, we conclude that the PAS spectra suffer from intensity distortion for the stronger absorption features. Further comparison of the IR-CRLAS data to the PAS data underscores the superior sensitivity of the ringdown apparatus. In the photoacoustic work, data were obtained with cell pressures of 12.5 Torr with a single pass absorption length of 45 cm. In Fig. 3, the cell pressure was 830 mTorr, with a single pass absorption length of 39 cm. As seen in the blowup of Fig. 3, the signal-to-noise ratio in the scan is about 1/2 that of the same spectrum shown in Ref. [3], indicating nearly an order of magnitude more sensitivity in the IR-CRLAS data when scaled for species concentration and cell length. These results constitute the first extension of CRLAS into the 1.6 $\mu$m region and demonstrate the high sensitivity and wide dynamic range (for absorption intensities) of the technique.

4.2. 3.3 $\mu$m region

In this section, we demonstrate the extension of IR-CRLAS into the 3.3 $\mu$m region with presentation of spectra of the $\nu_3$ fundamental band system of methane. This band was chosen as a proof of principle system because of its high line density (which will be further discussed in the next section) and to allow comparison with the direct absorption data obtained with difference frequency absorption spectroscopy [5]. The spectra were recorded under Doppler-limited conditions in a room temperature gas cell which was filled with $\approx 1.5$ mTorr of CH$_4$. Tunable light generated in the second OPA stage was coupled into the ringdown cavity with a simple telescope. Residual 1.6 $\mu$m light (<1% of total output) was filtered out with either a narrow bandpass filter or one of the ringdown mirrors used in the above work. The mirrors used in this region consisted of moderate reflectivity ($R = 99.2\%$) surface coated silicon substrates which were ground to a 6 m radius of curvature. The relatively low reflectivity of the mirrors used in this study resulted in decay times of hundreds of nanoseconds with an associated lower spectrometer sensitivity of $\approx 4 \times 10^{-4}$.

IR-CRLAS spectra of the Q-branch of the $\nu_3$ fundamental band of CH$_4$.
Fig. 4. IR-CRLAS spectra of the Q-branch region of the $\nu_3$ fundamental of CH$_4$, obtained under Doppler-limited conditions. The intensities of the absorption features are in excellent agreement with the high resolution absorption data of Ref. [5]. Total acquisition time for this 2 cm$^{-1}$ scan is $\approx 45$ min.

fundamental of CH$_4$ are shown in Fig. 4. In this scan, the laser was stepped at $\approx 0.0015$ cm$^{-1}$ per data point, with 25 shots averaged to reduce noise caused by preamplification of the InSb detector output. Comparison of the IR-CRLAS spectral intensities to those obtained in the absorption studies of Ref. [5] indicates excellent agreement among the data obtained with the two different techniques. In Ref. [5], direct absorption spectra were obtained with conventional absorption methods employing a cw difference frequency laser system with an experimental linewidth of $<0.0001$ cm$^{-1}$. The Doppler limited spectra ($p = 105$ mTorr) presented in that work (specifically, Fig. 1 of Ref. [5]) should be directly compared to the IR-CRLAS spectra of Fig. 4. The agreement of the relative intensities obtained in the two studies is excellent, with the exception of the overlapping $Q(5)_{F1}$ and $Q(4)_{F1}$ features in our data, which are more intense due to the greater overlap of the probe laser with the two transitions. An accurate comparison of the sensitivities in the two studies is not possible in this case, since the absorbance and associated noise level in Ref. [5] is not published, and raising the cell pressure in the present work to match that of Ref. [5] results in decay times which are too short to accurately characterize (i.e. too much absorption). In any case, the data presented above indicates the potential of the ringdown method for spectroscopic studies in the infrared. In this case, we anticipate improvements in the mirror reflectivity (closer to those in the 1.6 $\mu$m case) that will increase sensitivity in this spectral region by orders of magnitude. Closer inspection of the 3.3 $\mu$m data reveals important information about the ringdown method in general, which is specifically addressed in Section 5.

5. Interference effects – a test of the applicability of Fabry–Perot theories in pulsed ringdown spectroscopy

In this section, we experimentally explore the extent of longitudinal mode effects in the ringdown cavity and explicitly test some of the conclusions drawn in theoretical treatments. This issue is extremely important in the context of the applicability of the pulsed ringdown method, since at some point the cavity will behave like an etalon, and hence, may not be suitable for spectroscopic studies. This issue has been theoretically explored by us [8] and others [6,18], in some detail, but until now has never been experimentally addressed for the specific case of pulsed ringdown spectroscopy. In this work, the unique properties (e.g. pulse length and coherence length) of the laser system and ringdown cavity have been exploited to systematically search for the onset of interference phenomena. Although these studies are still in progress, we report here our preliminary results, which specifically demonstrate the ability to obtain quantitative absorption intensities in cases where the absorption linewidth is narrower than the longitudinal mode spacing of the cavity. Because a complete treatment of the theory of mode competition in optical resonators is beyond the scope of this Letter, the reader is referred to other sources where appropriate.

In order to investigate the effects associated with longitudinal mode effects in the ringdown cavity, two sets of experiments were performed. The first experiments were performed at 1.6 $\mu$m and consisted of constructing cavities of various lengths and scanning the single mode OPO over several free spectral ranges of the associated cavities, and looking for changes in the cavity transmission. The second set of experiments, performed at 3.3 $\mu$m, involved constructing cavities of different lengths and
measuring the absorption spectra of species introduced into the cavities. In this case, we ascertained whether absorption features would be distorted or missing, due to the cavity behaving like a comblike frequency filter, as is the case in intracavity laser absorption spectroscopy.

In these experiments, the single mode injection laser possesses a pulse duration of 3.5 ns fwhm (1.05 m in length) and a coherence length of ≈ 40 cm (125 MHz linewidth), with an associated absolute frequency stability of better than 50 MHz. In the first experiments, cavities ranging from 20 to 40 cm were constructed, such that the laser pulse coherence length was twice the cavity length and spatially overlapped with itself over five times (more than two cavity round trips) in the 20 cm cavity. In the limit of strict periodicity, the longitudinal mode spacing of the cavity is \( c/2L \), where \( L \) is the mirror spacing, resulting in a mode spacing of 750 MHz for the 20 cm cavity and 375 MHz for the 40 cm cavity, which in both cases is greater than the linewidth of the injection laser. If the cavity behaved like a comblike frequency filter, one would expect large variations in the transmission factor of the cavity as the laser was tuned to overlap with a cavity mode, based on simple Fabry–Perot models (see e.g. Ref. [19]). For all cavity sizes constructed in this range, the cavity was carefully aligned and the injection laser was scanned over 15 GHz (0.5 cm\(^{-1}\)), which is many times the cavity longitudinal mode spacing. In all cases, no significant changes in the cavity transmission coefficient were observed (to within 1% of the total transmissivity), indicating that the onset of interference effects had not occurred.

To further test these results and extend these studies to include the specific case of molecular absorption, gas cell cavities of 39 and 26 cm were constructed, with longitudinal mode spacings of 385 and 580 MHz, respectively. Spectra were obtained under Doppler-limited conditions, with associated linewidths of < 0.01 cm\(^{-1}\) (< 300 MHz). The spectra obtained with the 39 cm cavity was previously shown in Fig. 4, and consists of several Q-branch features of CH\(_4\). In this case, the injection laser and the absorption features are narrower than the mode spacing of the cavity, yet no intensity anomalies are observed. In fact, the absolute intensities agree within ≈ 10% of those obtained by Ref. [5], wherein the experimental linewidth was less than 1% of the Doppler limited linewidths. Spectra were also obtained with the 26 cm (580 MHz) cavity under similar methane concentrations (~ 1.5 mTorr partial pressure). In this case, the laser coherence length is twice the cavity length, overlaps with itself four times in the cavity, and the transition linewidths are < 1/2 of the cavity mode spacing. The partial results of these experiments are shown in Fig. 5, where the spectra recorded with the two different cavities are superimposed for comparison. Again, the same relative intensities are obtained and no significant intensity or lineshape anomalies (within < 10% fwhm) occur in the spectrum. In the work of Ref. [6], it was postulated that the ringdown cavity would exhibit significant interference effects in as few as two cavity round trips, regardless of the coherence length (bandwidth) of the injected light. In fact, they specifically predict that the transmission coefficient of the cavity would change by a factor of 4 for the case where the light overlaps for only two round trips (four passes), and conclude, in the case of molecular absorption, that the linewidth of the transition must therefore be wider than the longitudinal mode spacing of the cavity. In the case where the linewidth is less than the mode spacing of the cavity, they assert that the relative intensities would be distorted or that lines would be missing from the
spectrum, since it would be possible for the transition to fall between the longitudinal modes of the cavity. As can be seen in Figs. 4 and 5, no lines are missing, and the density of lines in the spectrum would make it impossible for all of the lines to fortuitously overlap with a cavity mode. Therefore, the absence of any pronounced intensity anomalies in our data is inconsistent with the conclusions drawn in Ref. [6]. These results are not too surprising, since it seems intuitively more reasonable that the onset of coherent effects should explicitly depend on 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 limitations of applying cw-based models to the pulsed regime. Experiments are currently underway in our laboratory to find the point at which coherent phenomena significantly distort the spectra obtained with the cavity ringdown method. At some point, the combination of cavity length, laser pulse length, and laser coherence length will lead to a situation in which the cavity behaves like an etalon, and subsequently may suffer from the aforementioned anomalies. However, the conditions under which this occurs as postulated by Ref. [6] are not consistent with our experimental data. This result bears important consequences for quantitative applications of the pulsed cavity ringdown method and demonstrates the validity of the exponential decay model in previously unexplored coherent regimes.

6. Summary

In this Letter, the first extension of the cavity ringdown technique into the infrared has been demonstrated in two spectral regions. This work indicates the generality of the ringdown method for infrared studies and underscores the potential of the technique for rapid survey scans and high resolution work. Experiments with cavities of various sizes and Doppler-limited absorption features have allowed the test of cw-based theories in pulsed ringdown experiments. Our data explicitly demonstrates the ability to obtain quantitative absorption data in cases where the absorption linewidths are much narrower than the free spectral range of the cavity, in direct contrast to the recent theoretical conclusions of Ref. [6].

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References