Microcavity Enhanced Raman Scattering

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Microcavity Enhanced Raman Scattering

by

Benjamin J. Petrak

A dissertation submitted in partial fulfillment of the requirements for the degree of
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DEDICATION

To the scientists that came before me.

I am only a small link in the chain of human discovery.
ACKNOWLEDGMENTS

First I would like to thank Dr. Andreas Muller and Dr. Nick Djeu who first conceived the idea for Purcell enhanced Raman scattering. Without their careful forethought and guidance none of this would have been possible. Next, I would like to thank my lab mates Kumarasiri Konthasinghe and Manoj Peiris for their help and support. I would like to thank James Christopher for his assistance in fabricating the parts necessary for our experiments. I would like to thank my family and friends for their support. And finally, I would like to thank the National Science Foundation and the Defense Threat Reduction Agency for their financial support.
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<td>PERS</td>
<td>Purcell enhanced Raman scattering</td>
</tr>
<tr>
<td>FP</td>
<td>Fabry-Pérot</td>
</tr>
<tr>
<td>s</td>
<td>Stokes</td>
</tr>
<tr>
<td>p</td>
<td>pump</td>
</tr>
<tr>
<td>as</td>
<td>anti-Stokes</td>
</tr>
<tr>
<td>CARS</td>
<td>coherent anti-Stokes Raman scattering</td>
</tr>
<tr>
<td>FSR</td>
<td>free spectral range</td>
</tr>
<tr>
<td>Q</td>
<td>quality factor</td>
</tr>
<tr>
<td>(\mathcal{F})</td>
<td>finesse</td>
</tr>
<tr>
<td>ROC</td>
<td>radius of curvature</td>
</tr>
<tr>
<td>PZT</td>
<td>piezoelectric transducer</td>
</tr>
<tr>
<td>FWHM</td>
<td>full width at half maximum</td>
</tr>
<tr>
<td>FPGA</td>
<td>field programmable gate array</td>
</tr>
<tr>
<td>TTL</td>
<td>transistor transistor logic</td>
</tr>
<tr>
<td>RMS</td>
<td>root mean squared</td>
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ABSTRACT

Raman scattering can accurately identify molecules by their intrinsic vibrational frequencies, but its notoriously weak scattering efficiency for gases presents a major obstacle to its practical application in gas sensing and analysis. This work explores the use of high finesse (∼ 50 000) Fabry-Pérot microcavities as a means to enhance Raman scattering from gases. A recently demonstrated laser ablation method, which carves out a micromirror template on fused silica—either on a fiber tip or bulk substrates—was implemented, characterized, and optimized to fabricate concave micromirror templates ∼ 10 µm diameter and radius of curvature. The fabricated templates were coated with a high-reflectivity dielectric coating by ion-beam sputtering and were assembled into microcavities ∼ 10 µm long and with a mode volume ∼ 100 µm$^3$. A novel gas sensing technique that we refer to as Purcell enhanced Raman scattering (PERS) was demonstrated using the assembled microcavities. PERS works by enhancing the pump laser’s intensity through resonant recirculation at one longitudinal mode, while simultaneously, at a second mode at the Stokes frequency, the Purcell effect increases the rate of spontaneous Raman scattering by a change to the intra-cavity photon density of states. PERS was shown to enhance the rate of spontaneous Raman scattering by a factor of $10^7$ compared to the same volume of sample gas in free space scattered into the same solid angle subtended by the cavity. PERS was also shown capable of resolving several Raman bands from different isotopes of CO$_2$ gas for application to isotopic analysis. Finally, the use of the microcavity to enhance coherent anti-Stokes Raman scattering (CARS) from CO$_2$ gas was demonstrated.
CHAPTER 1
INTRODUCTION

The need to accurately and quickly quantify concentrations of gases is paramount in modern society. Automation of manufacturing, the key to the inexpensive and widely available goods we rely on, is dependent on technological advances in sensing. Continuous monitoring of the chemical status in industrial processes, in a wide range of areas from fermentation to chemical manufacturing, is needed for consistent and efficient production [3]. Furthermore, monitoring of industrial exhaust is necessary for both high efficiency and environmental regulation [4, 5]. Advanced gas sensors could play a vital role in the context of global warming [6], and monitoring and investigation of pollutants [7, 8]. For example, an implementation of a cap and trade system for green house gases will require a reduction in the uncertainties in measurement of green house gas emissions [6]. Gas sensors have also invaded everyday life from medical diagnostics [9], to automotive sensors [10, 11], to indoor air quality monitoring [12]. The ever-increasing use of gas sensors in new and wide ranging areas will necessitate smaller and more robust systems.

Raman scattering, an inelastic scattering event first observed by C. V. Raman in 1928 [13], has proven to be a useful tool in gas sensing and analysis. The utility to gas sensing comes from the frequency shift experienced by Raman scattered light, which is determined by the rotational and vibrational modes of a particular molecule and therefore is a unique identifier. Due to its nondestructive nature, it can be used in situ and is capable of simultaneous multi gas analysis. Additionally, since the vibrational modes are a function of atomic mass, isotopologues can also be identified and, unlike infrared absorption, it is sensitive to homonuclear molecules. Despite its many positive attributes, the Raman signal
from gases is generally weak, with a scattering cross section of typically only $10^{-31} \text{cm}^2/\text{sr}$. Consequently, Raman scattering usually requires an enhancement for practical use.

Over the years a variety of techniques for overcoming the weak Raman scattering efficiency have been explored. Standard practice has been to increase the interaction path length through multi pass cells (i.e. resonant recirculation) [14, 15, 16, 17] and, more recently, hollow optical fibers [18, 19]. Other techniques that make use of the stimulated Raman method, such as coherent anti-Stokes Raman scattering (CARS), can yield larger signals, but involve complex setups [20]. And while surface enhanced Raman scattering (SERS), in which an enhancement occurs due to a surface plasmon resonance, has been shown to detect single particles [21, 22], it suffers from inconsistent reproducibility, slow adsorption and is inadequate for gas sensing [23].

In this work we explore a new route for the enhancement of Raman scattering. We make use of newly developed Fabry-Pérot (FP) microcavities to leverage two resonant phenomena, which combine to an enhancement of order $10^7$ compared to free space Raman scattering. Doubly resonant Purcell enhanced Raman scattering (PERS) occurs when the microcavity is resonant with both the pump and Raman emission frequencies. This takes advantage of both resonant recirculation of the pump light and Purcell spontaneous emission rate enhancement of the Raman scattered light.

As first shown by Purcell, the rate of spontaneous emission is not a fixed property of the emitter, but is determined by the local density of states of the electromagnetic field into which a photon can be emitted [24]. This phenomenon has been well studied with two-level fluorescence from atoms in an atomic beam by both inhibiting their spontaneous emission [25], and enhancing their rate of spontaneous emission [26, 27]. Subsequently, the Purcell effect was used to increase the rate of spontaneous Raman scattering from liquid benzene [28]. Following this, doubly resonant Purcell enhanced Raman scattering (PERS) was first shown in planar solid-state semiconductor cavities, where angle tuning of the pump beam was used to achieve the double resonance [29, 30], but for gas sensing, an open center FP cavity is required.
Recent advances in micromirror template fabrication by CO$_2$ laser ablation [31] have revolutionized the construction of FP microcavities. This has enabled a variety of experiments such as strong coupling in Bose-Einstein condensates [32], single atom detection [33] and fiber based opto-mechanical devices [34] or, in our case, enhancement of Raman scattering from a gas. The FP microcavities constructed from these templates are ideally suited for our experiments. The high finesse ($\approx 50000$) provides strong resonant recirculation and the cavity’s small mode volume ($\sim 100$ $\mu$m$^3$) is an essential requirement for the Purcell effect. Furthermore, the open center allows the free flow of sample gases. With this setup we were able to detect Raman scattering from CO$_2$ in ambient air (400 ppm) in seconds with only $\approx 10$ mW of pump power and using only a minute sample volume.

This document will first review our micromirror template fabrication setup, which resulted in the publication of “Feedback-controlled laser fabrication of micromirror substrates” [Petrak et al. Rev. Sci. Instrum. 82, 123112 (2011)]. Next, it will discuss the construction of our FP microcavity and our experimental setup and then introduce the theory needed for our Raman enhancement experiments. Third, it will review the two Purcell enhanced Raman scattering experiments, which resulted in two papers “Purcell-enhanced Raman scattering from atmospheric gases in a high-finesse microcavity” [Petrak et al. Phys. Rev. A 89, 023811 (2014)] and “Isotopic gas analysis through Purcell enhanced Raman scattering” [Petrak et al. Appl. Phys. Lett. 108, 091107 (2016)]. The next chapter will review the enhancement of the coherent anti-Stokes Raman scattering signal in our microcavity, which resulted in the paper “Coherent Anti-Stokes Raman Scattering in a High-Finesse Microcavity” [Petrak et al. Opt. Express 22, 21999 (2014)]. Finally, the last chapter will discuss peripheral phenomena and potential future directions in microcavity PERS research.
CHAPTER 2
MICROMIRROR TEMPLATE FABRICATION

2.1 Introduction

The micromirror fabrication process starts with the creation of micromirror templates. This is done by a recently established ablation technique [31] in which a fixed energy pulse from a CO\textsubscript{2} laser is focused onto a substrate and then carves out a small (∼100 µm) diameter indentation. Reflow of material during ablation creates an ultra smooth surface, which is then coated to form a concave mirror. Two micro mirrors can then be assembled to form a micro Fabry-Pérot cavity of high finesse (∼100000).

![Fabrication process](image)

Figure 2.1. Fabrication process: 1) A CO\textsubscript{2} laser pulse is focused onto a substrate. 2) Ablation forms a concave indentation. 3) The template receives a high reflectivity dielectric coating to form a mirror.

2.2 Fabrication Setup

Our micromirror fabrication setup used a radio-frequency (RF) excited Synrad\textsuperscript{TM} CO\textsubscript{2} laser with a wavelength of 10.6 µm. The laser was controlled by a transistor-transistor-logic (TTL) pulse sequence with a signal period of 200 µs. To generate the TTL pulse sequence,
a field programmable gate array (FPGA) was used. The laser was kept in a ready state by “Tickle” pulses 1 µs long at a rate of 5 kHz. To generate a laser pulse, a “Tickle” pulse was replaced with a square RF pulse at a variable percent of the duty cycle. The “Tickle” pulse directly after a laser pulse was removed to prevent unwanted laser output. Fig. 2.2 depicts a 50 µs square RF pulse along with the laser’s output intensity. The typical laser pulses used were between 40 µs and 200 µs.

![Figure 2.2](image-url)  
Figure 2.2. Temporal evolution of fixed pulse operation.

We found that under fixed pulse operation there was a higher than optimal level of variability in micromirror template size and that the intensity of white light emitted during the ablation process is increasing with the size of the ablated feature. This is displayed in Fig. 2.3.

![Figure 2.3](image-url)  
Figure 2.3. Peak emitted white light plotted vs. feature diameter.
To take advantage of this, we modified the FPGA programming to setup a feedback loop during ablation. A Si photodetector was mounted behind the sample such that it would detect the white light emitted during ablation (for fabrication on the tip of an optical fiber, the detector was placed at the other end of the fiber). The voltage from the detector, \( V_{\text{det}} \), was sent to a comparator which was then compared to a user set voltage, \( V_{\text{ref}} \), that was determined by the desired feature size. With the laser in ready mode, the process was started by a high TTL signal to the laser from the FPGA. This prompted the laser output. When \( V_{\text{det}} > V_{\text{ref}} \), the comparator sent a signal to the FPGA which sent the “Tickle” signal to the laser to return it to a ready state and stop laser output. The temporal evolution of the feedback process is represented in Fig. 2.4.

![Fig. 2.4. Temporal evolution of feedback controlled operation. The top black is the ttl signal and the red is the intensity output of the laser. The middle black is the reference set by the user and the green is the voltage from the photodetector. The bottom is the signal from the comparator that stops the laser output. Note: it is only high when the photo detector voltage exceeds the reference voltage, but the ttl is set to low at the instant the comparator gives a high signal.](image)

To quantify the reduction in size variability due to operation with feedback, we measured the RMS feature diameter size fluctuation, 
\[
\Delta D_{RMS} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (D_i - \overline{D})^2},
\]
where \( \overline{D} \) is the mean diameter. With fixed power operation, we obtained \( \Delta D_{RMS}/\overline{D} = 50\% \).
and with feedback loop operation we obtained $\Delta D_{RMS}/D = 4\%$. The top of Fig. 2.5 displays a sample of six of the examined templates from both feedback controlled and fixed pulse operation. The bottom of Fig. 2.5 shows the measured diameter for each feature with the average in solid red and $\Delta D_{RMS}$ in dashed red.

Figure 2.5. Top: Optical microscope image of six samples with feedback on the left and without feedback (fixed energy pulse of $\approx 270\mu J$) on the right. The blue circles are from a Hough transform circle recognition program. Bottom: Measured diameter for all samples with feedback on the left and without feedback on the right. The red line is the mean and the dashed red line is $\Delta D_{RMS}$.

The CO$_2$ laser produced a linearly polarized beam with a spot size of $w = 4$ mm and wavelength of $\lambda = 10.6$ $\mu$m. To finely adjust the intensity of the beam, a polarizer was placed in its path. The polarizer’s angle could be rotated to produce the desired output intensity. A ZnSe lens, with $f = 25.4$ mm, was used to focus the beam on the sample with an estimated spot size at the focus of $w = 20$ $\mu$m. A flip mounted mirror was placed just after the ZeSe lens. A second lens was positioned such that, when the mirror was flipped up, it focused on the sample and allowed us to image the sample and position it to
create a micromirror template in the desired location after the mirror was flipped down. This was crucial for templates created on the tip of an optical fiber, which needed to be centered on the fiber core. The setup is depicted in Fig. 2.6 with both planar substrate and fiber tip operation.

![Diagram of mirror fabrication setup]

Figure 2.6. Mirror fabrication setup: (a) Planar substrate operation (b) Fiber tip operation.

### 2.3 Mirror Template Characteristics

Ten mirror templates were examined with an AFM. To get a measurement of the surface micro roughness, the difference from a parabolic fit to a cross section, dashed line in Fig. 2.7(a), was calculated. A surface micro roughness for all ten of $\sigma_{RMS} \leq 0.2$ nm was found, which was the limit of resolution of the AFM used and is likely lower than this. Furthermore, a radius of curvature (ROC) of 90 $\mu$m was extrapolated from one fit. A set of mirror templates of various sizes was fabricated on both planar substrates and optical
fibers and was coated by ion beam sputtering with a high reflectivity (R = 99.995% at 940 nm) dielectric coating.
CHAPTER 3
FABRY-PÉROT MICROCAVITY

3.1 Introduction

This chapter will first introduce the needed basic background for Fabry-Pérot cavities. Then it will move on to the cavity assembly and experimental setup, which will include the experimental characterization of the cavity and mirrors. Finally, it will conclude with a description of two microcavity effects that will be exploited for our scattering experiments—resonant recirculation and the Purcell effect.

3.2 Cavity Basics

An optical resonator, or cavity, spatially confines light. Although there are many different geometries in which light can be confined, this discussion will be limited to Fabry-Pérot cavities. Starting with a cavity formed by two planar mirrors with the same power reflectivity $r^2 = R$ and separated by a distance $L$, the intensity of a transmitted plane wave at a wavelength $\lambda$ through the cavity is given by

$$I_t = \frac{(1 - R)^2}{(1 - R)^2 + 4R \sin^2(\frac{2\pi n L}{\lambda})},$$

(3.1)

where $n$ is the index of refraction of the intra-cavity gas, which will be set equal to 1 for simplicity. The free spectral range (FSR) is the separation, in frequency, between longitudinal modes (or where the transmission is maximum) and the linewidth, $\Delta \nu$, is the full width at half maximum (FWHM) of transmission peaks. In the absence of frequency-dependent mirror phase shifts and gas dispersion, the FSR is given by
From Eq. (3.1) a common figure of merit for a cavity, the finesse ($\mathcal{F}$), is derived. The finesse, related to the quality factor ($Q$) by $Q = 2\mathcal{F}L/\lambda$, is, in the absence of losses, given by

$$\mathcal{F} = \frac{\pi \sqrt{R}}{1 - R} = \frac{FSR}{\Delta\nu}. \quad (3.3)$$

Eq. 3.1 gives the maximum transmission when $L = m\lambda/(2\pi)$, where $m$ is a positive integer associated with a longitudinal mode (cavity resonance). On resonance, the half round-trip phase shift is defined by

$$kL = m\pi \quad (3.4)$$

where $k = 2\pi/\lambda$. 

Figure 3.1. Transmission by a planar cavity.
In practice, diffraction losses set a limit on the maximum finesse achievable with a planar cavity. Curved (concave) mirrors must be used to achieve a finesse beyond \( \approx 1000 \).

A cavity constructed with concave mirrors supports Gaussian beams.

Gaussian beams have a radial intensity profile of a Gaussian [36] and the complex electric field of the fundamental Gaussian beam, for a wavelength \( \lambda \), is given by

\[
u(r, z) = \frac{w_0}{w(z)} \exp(-i(kz - \Phi) - r^2(\frac{1}{w(z)^2} + \frac{ik}{2R(z)})), \tag{3.5}\]

where \( k = \frac{2\pi}{\lambda} \) is the \( z \)-component of the wave vector. \( R(z) \) is the radius of curvature of the wavefront that intersects the axis at \( z \) and is given by

\[
R(z) = z(1 + \frac{z^2}{2R}) \tag{3.6}
\]

and the distance, from the \( z \)-axis, where the field amplitude is \( 1/e \) times the value on the axis is \( w(z) \), the spot size, which is given by

\[
w(z)^2 = w_0^2(1 + \frac{z^2}{2R}). \tag{3.7}\]

The beam diameter is \( 2w \), with the minimum beam diameter, \( 2w_0 \), known as the beam waist. Like with the plane wave there is a phase shift of \( kz \), but unlike the plane wave there is an extra phase shift term

\[
\Phi(z) = \arctan(\frac{\lambda z}{\pi w_0^2}), \tag{3.8}
\]

which is called the Gouy phase shift. The term \( z_R \) is the Rayleigh range, which is defined by

\[
z_R = \frac{\pi w_0^2}{\lambda}. \tag{3.9}\]

In reality Eq. 3.5 is just one of a set of “modes of propagation” that fully describe a Gaussian beam. The full set is made up of Hermite-Gaussian functions in rectangular
coordinates or Laguerre-Gaussian functions in cylindrical coordinates. These modes form a complete and orthogonal set of functions and they can describe any arbitrary distribution of monochromatic light. The modes of propagation are referred to as transverse electromagnetic or TEM modes with subscripts, known as mode numbers, that identify the order of polynomials used. Eq. 3.5 is the TEM$_{00}$ or fundamental mode. The boundary conditions imposed by a cavity govern the modes of propagation of a Gaussian beam within the cavity. Four Hermite-Gaussian modes for a cavity of rectangular geometry are plotted in Fig. 3.2. Each mode of propagation, within a confocal cavity, has a different round-trip phase shift and, therefore, its own resonate frequency. For simplicity, this document will focus solely on the fundamental mode for all calculations involving Gaussian beams within a cavity.

Figure 3.2. Hermite-Gaussian mode patterns in rectangular symmetry. Calculated using [1]
Now that Gaussian beams have been defined, we can talk about our Fabry-Pérot cavity, which is constructed from concave spherical mirrors. In this case, we can take Eq. 3.5 and impose the condition that $R(z)$, at mirror potions $z$ and $-z$, matches the mirrors’ ROC and, for simplicity, we set the ROC for both mirrors to be equal to $R$. If we define the separation of the mirrors to be $L$ then

$$w_0^2 = \frac{\lambda}{2\pi} \sqrt{L(2R - L)},$$

(3.10)

which gives the beam waist in the middle of the cavity, which, along with 3.5, defines the field within the cavity. The intra-cavity field is depicted in Fig. 3.3.

![Intra-cavity Gaussian beam](image)

Figure 3.3. Intra-cavity Gaussian beam.

Resonance occurs when the half trip phase change is a multiple of $\pi$.

$$kL - \Phi(L) = m\pi$$

(3.11)

This is just half of the round trip phase from the planar cavity, Eq. 3.4 with a length of $L$, minus the Gouy phase, Eq. 3.8.

### 3.3 Microcavity Assembly

The micromirrors were assembled into concave Fabry-Pérot microcavities with each microcavity formed by one micromirror on a fiber tip and one micromirror on a planar
substrate. We used two different styles of cavity assemblies. Both made use of two piezoelectric transducers (PZT) to vary the cavity length, with one PZT for long range offset and the other for scanning around a resonance and locking to the pump laser. The first cavity assembly, shown in Fig. 3.4(a), used a mechanical flexure design to amplify the action of the PZTs. This design provided a larger tuning range, but was more sensitive to disturbances when locked to the pump. The second design, Fig. 3.4(b), directly uses the action of the PZTs, this results in a more stable monolithic assembly, but with the cost of a reduced overall displacement. Both assemblies used an aspheric lens for mode matching an incoming laser beam (and collimating outgoing light) through the planar substrate side and had a sealed chamber, around the cavity, into which we could flow the sample.

![Figure 3.4](image)

Figure 3.4. (a) Model of the flexure amplified assembly. (b) Picture of the monolithic direct action assembly with cross sectional a diagram of the internal makeup superimposed.

### 3.3.1 Assembly Construction

The mirrors were permanently bonded to the cavity assembly. To do this, both mirrors were roughly positioned into the assembly and wet epoxy was applied. To finely align the mirrors, a laser was sent through the fiber end and the transverse cavity modes were viewed through the lens on the planar side. Then the z position of the fiber mirror and the x-y position of the planar mirror were adjusted to the $TEM_{00}$ mode—see Fig. 3.3. Once
aligned, it was left overnight to let the epoxy dry. After drying, the assembly was secured in a box that provided stability from local air currents. The box also contained a Peltier tile for thermal stability and tubing for sample gas in and out flow.

Figure 3.5. Direct action cavity assembly secured in a protective box.

3.4 Experimental Setup

The box was then placed in our experimental setup. In this setup we have two tunable diode lasers (Toptica DL pro) with linewidth $\approx 1$ MHz. One with a range from 862 to 924 nm, which will serve as the pump laser, and the other with a range of 906 to 993 nm will be used as a reference to aid in tuning to the double resonance. The higher wavelength laser (reference laser) is sent into the cavity via a flip mounted mirror so that, after tuning to the double resonance, we can flip down the mirror and direct the Stokes emission from the cavity into a fiber, which is then sent to a spectrometer. We estimate a total collection efficiency of $\approx 1\%$, which includes the propagation and filter losses as well as the quantum efficiency of the detector (note: the microcavity CARS experiments did not use a spectrometer and therefore had slightly less propagation losses). The cavity can
be locked to the pump laser through transmission collected from the optical fiber side or in reflection off the planar substrate side. For characterization of the cavity we can use both lasers to access a broad range of frequencies. We have set up a polarizing beam splitter and a quarter wave plate in the path of each laser so we can separate the reflection from the input for analysis. We can also monitor the transmission through the fiber side. Fig. 3.6 shows a picture of our setup with beam paths overlaid on it. This setup is common to both PERS experiments except we also made use of a Ti:sapphire laser for the pump in the isotopic analysis experiments. The setup is slightly modified for coherent anti-Stokes Raman scattering as we use the tuning laser for the generation of the anti-Stokes wave after tuning to the double resonance.

Figure 3.6. Experimental setup.

3.5 Mirror Characterization

To characterize the mirrors, we measured the transmission of a fixed frequency laser beam through our Fabry-Pérot while scanning the mirror separation over one FSR (Eq. 3.2). This way we could extract the finesse as FSR/FWHM (Eq. 3.3). We measured a peak finesse of $F \approx 58\,000$ at 940nm as shown in Fig. 3.7.
Figure 3.7. (a) Scan over two longitudinal modes. (b) Close-up of one resonance which shows splitting due to coating birefringence and mirror geometry.

Figure 3.8. Reflectivity plot of mirrors over the high reflectivity bandwidth with points representing the experimental values and the curve representing the theoretical values.

The same procedure was repeated for several wavelengths within the high reflectivity band of the cavity and the experimentally obtained values for reflectivity are plotted in Fig. 3.8 along with the theoretical reflectivity calculated from the specification of the dielectric coating.
3.6 Cavity Effects

Described in this section are the two effects that are simultaneously exploited under the cavity double resonance. First is the enhancement of pump beam’s intensity due to resonant recirculation inside the cavity. The second is the increase in the rate of spontaneous emission provided by the Purcell effect.

3.6.1 Circulating Intensity

The intensity of light, on resonance, circulating inside the cavity can be orders of magnitude larger than the intensity of the light incident on the cavity. The circulating signal is made of the sum of light transmitted and the round trip circulating light that has reflected off of both mirrors. Assuming negligible absorption, the ratio of circulating intensity to incident intensity is given by [37]

\[ \frac{I_{\text{circ}}}{I_{\text{inc}}} = \left| \frac{1}{t} \right|^2 = \frac{1}{T} = \frac{1}{1 - R} \approx \frac{F}{\pi}. \] (3.12)

This means the power inside the cavity is a factor of \( \frac{F}{\pi} \) increased over the incident power.

3.6.2 Emission Rate Enhancement

The rate of spontaneous emission is not solely a property of an atom, but one of both the atom and the field with which it interacts. The local density of states, into which an atom in an excited state can emit a photon, can enhance or even decrease the emission rate. This can easily be seen for the case of an excited two level atom interacting with the vacuum field starting from Fermi’s Golden rule [38]

\[ \frac{1}{\tau} = \frac{2\pi}{\hbar^2} |M_{12}|^2 \rho(\omega_e) \] (3.13)

where \( \tau \) is the lifetime, \( M_{12} \) is the transition matrix element and \( \rho(\omega_e) \) is the density of states at the emission frequency. This gives the rate of emission, which is proportional to the density of states.

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The density of states within a Fabry-Pérot cavity is given by [38]

\[
\rho(\omega)_{\text{cav}} = \frac{2}{\pi} \frac{\Delta \omega_c}{4(\omega - \omega_c)^2 + \Delta \omega_c^2}
\]  

where \( \Delta \omega_c = 2\pi \Delta \nu_c \) is the cavity linewidth and \( \omega_c \) is the resonant frequency. At the resonant frequency, the magnitude of Eq.(3.14) is dependent on the linewidth and therefore the reflectivity of the mirrors. The density of states for free space, a low finesse cavity and a high finesse cavity are plotted on Fig. 3.9. It is clearly seen that in a cavity on resonance the density of states and the rate of emission is higher than that of free space. Furthermore the effect is greater in a higher finesse cavity. Also, on the tails of the Lorentzian, the density of states is near zero and emission can be suppressed.

![Figure 3.9. Density of states for: free space (free), low finesse cavity (cav a), and a high finesse cavity (cav b).](image)

If we use the electric dipole approximation for the matrix element, we can get the ratio of the rate inside a cavity to that in free space, which is commonly called the Purcell factor [24]. With the dipoles oriented along the field direction and the cavity on resonance with the emission frequency, the Purcell factor is given by

\[
F = \frac{\rho(\omega)_{\text{cav}}}{\rho(\omega)_{\text{free}}}
\]
\[ F_p = \frac{\tau_{\text{free}}}{\tau_{\text{cav}}} = \frac{3Q(\lambda/n)^3}{4\pi^2 V_{\text{eff}}} \]  

(3.15)

where \( Q \) is the cavity quality factor, \( n \) is the index of refraction and \( V_{\text{eff}} \) is the effective mode volume of the cavity. As is seen by Eq. (3.15), the enhancement is directly proportional to the quality factor and inversely proportional to the mode volume of the cavity. Hence, high finesse and small mode volume cavities produce a high spontaneous emission enhancement. The Purcell factor can be generalized to other light matter interactions including Raman scattering [39].
CHAPTER 4
PURCELL ENHANCED RAMAN SCATTERING (PERS)

4.1 Introduction

This set of experiments makes use of the high finesse Fabry-Pérot microcavities for the enhancement of spontaneous Raman scattering. In these experiments a confocal Fabry-Pérot microcavity was tuned to be resonant with both the pump and Stokes frequencies—a double resonance. Raman scattering within the cavity experienced an enhancement of order $10^7$ compared to free space emission into the same solid angle. These results demonstrate the potential of this technique for use in a practical gas sensing system.

4.2 Theoretical Discussion

4.2.1 Spontaneous Raman Scattering

Spontaneous light scattering occurs when light interacts with a material. During the scattering process an incident photon is absorbed while, simultaneously, a scattered photon is emitted. Raman scattering occurs when the incident photon interacts with the rotational and/or vibrational modes of the molecules in the scattering medium. If the molecule is initially in the ground state, then the incident photon will excite the molecule to a higher energy level and the scattered photon will be down shifted in energy, which is referred to as Stokes scattering. Anti-Stokes scattering, when the molecule is initially in an excited state and the scattered photon is up shifted in energy, is just the opposite. Rayleigh scattering is when the incident photon has the same frequency as the scattered photon. The photon’s change in energy is called the Raman shift and is given by
\[ \Delta E_V = h\nu_i - h\nu_s \]  

(4.1)

where \( h \) is Planck's constant and \( \nu_i \) is the initial photon’s frequency and \( \nu_s \) is the finally photon’s frequency. The change in frequency, the Raman shift, is given by

\[ \Delta \nu_V = \nu_i - \nu_s. \]  

(4.2)

The energy diagram is depicted in Fig. 4.1 (a) along with an idealized spectrum in Fig. 4.1 (b).

(a)

(b)

Figure 4.1. (a) Energy diagram of Raman scattering (b) Idealized spectrum from Raman scattering with relative intensities (not to scale).

As can be seen from the spectrum, the Raman signal is weaker than the Rayleigh signal. Furthermore, due to the thermal distribution of energy states, most of the molecules are in the lower state at room temperature and Stokes scattering is stronger than anti-Stokes. In Eq. 4.1 and Eq. 4.2, and the rest of this text, the “s” subscript stands for Stokes and the “as” for anti-Stokes. A more detailed quantum mechanical description of spontaneous
Raman scattering, in which the rate of free space scattering is calculated, can be found in appendix C. The Raman shift, Eq. (4.2), and resonance lineshape are dictated by the vibrational and rotational energy levels of a molecule (see appendix E), which are determined by the geometry and make up of the molecule. This means that the Raman shift is a unique “finger print” for a molecule, which we take advantage for our gas sensing experiments.

4.2.2 PERP Conceptual Picture

The enhancement of Raman scattering is attributed to two cavity effects, which produce three enhancement effects. The first is due to the resonant recirculation, Eq. (3.12), of light inside the cavity. When the cavity is resonant with the pump frequency, at longitudinal mode $m_p$, there is a build up of pump light. This increased pump intensity is proportional to the cavity’s finesse, Eq. (3.3), and is a property of all Fabry-Pérot cavities- macro or micro. The augmented pump intensity leads to increased Raman scattering, which is expected and a common method of scattering enhancement [16, 17]. The second effect, known as the Purcell effect, increases the rate of spontaneous emission. This happens because confinement of the electromagnetic wave, at the Stokes frequency at cavity mode $m_s$, increases the density of states into which the molecule can scatter light as described in section 3.6.2. This effect is washed out in large cavities and necessitates a microscopic cavity. The third effect, which is a part of the Purcell effect, is an enhancement to the collection of scattered light. Since the scattered light is coupled to cavity mode $m_s$, virtually all scattered light exits through the cavity mode and out the mirrors to be collected. When the cavity is tuned to be resonate with the pump and Stokes frequencies, all three enhancement effects happen simultaneously. Hence, we get increased scattering at a faster rate with better collection efficiency.
4.2.3 Double Resonance Condition

To achieve a Raman double resonance, the mirror separation must be set such that the Raman shift is equal an integer number of free spectral ranges (FSR). In this scheme, the pump is coupled to one longitudinal cavity mode with mode number \( m_p \) and the Stokes Raman emission is coupled to another longitudinal mode with mode number \( m_s \). The condition for cavity resonance is set by the half trip phase shift. To take into account the effects of the mirrors, the frequency dependent phase shift experienced from reflection off the mirrors, \( \varphi(\nu) \), is added into Eq. 3.11. This gives the new half trip phase shift

\[
kL - \Phi(L) + \varphi(\nu) = m\pi, \tag{4.3}
\]

where \( k \) is the wave number and \( \nu \) is the resonance frequency.

Figure 4.2. (a) Calculated microcavity frequency comb with the pump (red) and Stokes (green) plotted over their respective longitudinal modes. (b) Diagram of the cavity with the spontaneous Raman scattering energy diagram superimposed.

If we take Eq. (4.3) and solve for the resonance frequency \( \bar{\nu} \), in wave numbers (cm\(^{-1}\)), for the pump and Stokes emission and then take the difference, we get the condition for the Raman double resonance as
\[ \Delta \nu_V = \frac{1}{2L} \left[ \frac{m_p}{n} - \frac{m_s}{n'} \right] + \frac{\Phi(L)}{\pi} \left( \frac{1}{n} - \frac{1}{n'} \right) - \frac{1}{\pi} \left( \frac{\varphi(\bar{\nu}_p)}{n} - \frac{\varphi(\bar{\nu}_s)}{n'} \right) \], \quad (4.4) 

where \( n \) and \( n' \) are the respective refractive indices in air and \( \Delta \nu_V \) is the Raman shift. Since \((n - n') < 10^{-7}\), the term involving the Gouy phase shift, \( \Phi(L) \), can be ignored. Then we can solve for the optimal length and frequencies. To visualize the double resonance, the frequency comb of the doubly resonant microcavity along with the pump and the Raman emission superimposed on it is shown in Fig. 4.2(a).

4.2.4 Peak Rate Calculation

To get an idea of the expected enhancement, we first set all indices of refraction equal to one for simplicity and then start with the rate equation for Stokes photons scattered into a single free space mode, \( \frac{dn_s}{dt} = Dn_p \) [Eq. (C.10)]. Next, we convert this to the rate equation for Stokes photons scattered into a single cavity mode by subtracting the Stokes photon cavity decay rate, \( n_s/\tau_c \), from the right hand side to get

\[ \frac{dn_s}{dt} = Dn_p - \frac{n_s}{\tau_c}, \quad (4.5) \]

where \( n_s \) is number of Stokes photons scattered into cavity mode \( m_s \) by \( n_p \) pump photons in cavity mode \( m_p \) with \( \tau_c \) representing the Stokes photon cavity lifetime and \( D \) is a constant. Next we set \( D = F_p/\tau_R \) to get

\[ \frac{dn_s}{dt} = \frac{F_p}{\tau_R} n_p - \frac{n_s}{\tau_c}, \quad (4.6) \]

where the spontaneous Raman “lifetime” in free space, \( \tau_R \), for \( N \) particles per unit volume with a differential scattering cross section of \( d\sigma/d\Omega \) is

\[ \tau_R^{-1} = \frac{8\pi \nu_p}{3 \nu_s} NC \frac{d\sigma}{d\Omega}, \quad (4.7) \]

with \( c \) being the speed of light and the Purcell factor, \( F_p \), calculated in [39] is given by
The pump and Stokes frequencies are given by \( \nu_p \) and \( \nu_s \) (the respective wavelengths are \( \lambda_p \) and \( \lambda_s \)), the Raman linewidth is \( \Delta \nu_R \) and the cavity linewidth at the Stokes frequency is \( \Delta \nu_c^{(s)} \). The effective mode volume, \( V_{\text{eff}} \), which takes into account the overlap of pump and Stokes modes, is also calculated using [39] and is given by

\[
V_{\text{eff}} = \frac{(\lambda_p + \lambda_s)}{\tan^{-1}[L/\sqrt{2(R - L/2)L}]},
\]

(4.9)

where \( R \) is the radius of curvature of the mirrors. The calculation of the PERS effective mode volume can be found in appendix B.1. Now we take Eq. (4.6) at a steady state and solve for \( n_s/\tau_c^{(s)} \), which is the rate of the number of Stokes photons exiting the cavity. Since we are collecting from only one side of the cavity we take half of the result and use \( n_p = 2P_{\text{in}}\tau_c^{(p)}/h\nu_p \) and \( \tau_c^{(p)} = 1/(2\pi\Delta \nu_c^{(p)}) \) to get a rate of emission of

\[
\gamma_{\text{cav}} = \frac{Nc\lambda^2 P_{\text{in}} \tau_c^{(p)}}{\pi h V_{\text{eff}}} \frac{d\sigma}{d\Omega} \frac{\Delta \nu_R + \Delta \nu_c^{(s)}}{\Delta \nu_c^{(s)}},
\]

(4.10)

where \( P_{\text{in}} \) is the pump input power.

### 4.2.5 Double Resonance Lineshape

Due to the scanning of both the cavity length and the pump frequency over the Raman spectrum, the double resonance linewidth is a convolution of the cavity lineshape and the Raman resonance lineshape and is given by

\[
\gamma_{\text{cav,DR}}(\nu_p) = \left( \frac{\nu_p}{\Delta \nu_c^{(s)}} \right)(\Delta \nu_R + \Delta \nu_c^{(s)}).
\]

(4.11)

The calculation of 4.11 can be found in appendix B.2. The closed analytical expression in Eq. 4.11 assumes a Lorentzian lineshape for the Raman band, but in general this is not the case.
When a Lorentzian lineshape for the Raman band cannot be assumed, one can simulate data by assuming a Lorentzian lineshape for each ro-vibrational line \((J = 1, 2, 3, \ldots)\) in the band. Then using experimentally obtained physical constants from [40] for \(B\) and \(D\) along with Eq. E.14,

\[
\tilde{\nu}_J = \tilde{\nu}_0 + J(J + 1)(B'_\nu - B''_\nu) + J^2(J + 1)^2(D''_\nu - D'_\nu)
\]  

(4.12)

where \(\tilde{\nu}_0\) is the Raman shift and the single and double primes denote the upper and ground vibrational states, to get each ro-vibrational line’s position in frequency and Eq. E.12,

\[
I_J = \left(\frac{hcB''_\nu}{kT}\right)(2J + 1)e^{-B''_\nu J(J+1)hc/kT}
\]  

(4.13)

where \(T\) is the temperature and \(k\) Boltzman’s constant, to get their relative intensities, each individual line can be calculated. The summation of each individual ro-vibrational line gives an accurate representation of the actual Raman band lineshape. Next, the effects of the cavity can be included by applying a convolution of the cavity lineshape, modeled by a Lorentzian, with the previously calculated Raman band lineshape. A detailed description of these equations can be found in appendix E.

4.3 Single Gas Sensing

4.3.1 Experimental

Without loss of generality, we focused our studies on the carbon dioxide molecule. \(\text{CO}_2\) has several vibrational transitions, of which, the upper component, \(\nu_+\), from the Q-branch of the \(2\nu_2/\nu_1\) Fermi dyad (For a description of this notation see appendix E section E.0.2.) with \(\Delta\tilde{\nu}_V = 1388.17 \text{ cm}^{-1}\) was chosen for our initial experiment. In order to fulfill the double resonance condition described above by Eq. (4.4) for \(\Delta\tilde{\nu}_V = 1388.17 \text{ cm}^{-1}\), the calculated cavity length is \(L = 26.22 \mu\text{m}\) with the pump mode number \(m_p = 61\) and the
Stokes mode number $m_s = 54$. The frequency of the pump laser was calculated to be $\nu_p = 11539.47 \text{ cm}^{-1}$, which produces Raman emission at $\nu_s = 10151.40 \text{ cm}^{-1}$.

Fig. 4.3 shows the layout of the single gas experiment. In this experiment we utilized the mechanically amplified flexure cavity assembly [3.4(a)] which allowed gas with different premixed concentrations of CO$_2$ (the balance of which was “air”: 80% N$_2$ and 20% O$_2$) to be continuously flowed through the microcavity during the experiment.

In order to tune the cavity to the double resonance length, a reference laser was used, spatially overlapped with the pump laser by use of a dichroic mirror, and maintained at a constant frequency separation from the pump corresponding to the Raman shift. This way, with Eq. (4.4) as a guide, the double resonance could be found experimentally. After the double resonance was located, the reference laser was shut off and the path from the cavity to it was redirected with a flip mounted mirror into a grating spectrometer to analyze the Raman emission. Then the cavity length was locked to the pump laser, using a Pound-Drever-Hall (PDH) locking scheme (Section F.1.2), and the laser was scanned over the full line shape of the Raman emission. Data was collected for four concentration of CO$_2$ in air– 100%, 1%, .1% and .04% (400 ppm in ambient air).
Figure 4.4. Raman emission rate for the four concentrations of CO\textsubscript{2} gas in air as a function of pump laser frequency. The traces have been scaled and offset for clarity. The inset shows the peak transmission as a function of CO\textsubscript{2} concentration.

The spectra for the four concentration of CO\textsubscript{2} in air are displayed in Fig. 4.4. The peak rate for 100% CO\textsubscript{2} is $\approx 10^8$ photons/s, which is on the same order as the prediction made by Eq. (4.10), namely $2.3 \times 10^8$ photons/s, corresponding to a $\sim 10^7$ enhancement compared to free space Raman scattering for the same volume of gas collected by the solid angle subtended by the cavity. The difference in resonant frequency between the 100% CO\textsubscript{2}
sample and the samples that consist of 99% or more “air” is due to the difference in index of refraction between “air” and CO$_2$ gas which is approximately one part per thousand.

4.3.2 Conclusion

Using a state-of-the-art micro mirror fabrication process we constructed concave micro mirrors and assembled them into high finesse FP microcavities. These FP microcavities provided an enhancement to Raman scattering of $\sim 10^7$ compared to the same volume of gas in free space. This allowed us to obtain a measurable signal from CO$_2$ in ambient air (400 ppm) at a rate of $\sim 10^4$ photon/s.

4.4 Isotopic Analysis

4.4.1 Introduction

In this microcavity experiment we demonstrate the utility of PERS for isotope analysis. Because the ratios of isotopes in a material can differ due to factors such as location (on earth) of and method of synthesis, the analysis of the ratios of isotopes has application to several branches of science from atmospheric science [41, 42] to forensics [43]. Furthermore, the ratios can be artificially manipulated to extract information such as in the case of medical diagnostics [44, 9, 45], where isotopic tracers are used. Despite the wide array of uses, most rely on mass spectrometry, which requires a high level of sample preparation, is expensive and its large size precludes it from miniaturization [46]. PERS offers a low cost compact alternative.

4.4.2 Experimental

Without loss of generality, we investigated the three most common isotopologues of CO$_2$ gas: $^{12}$C$^{16}$O$_2$, $^{13}$C$^{16}$O$_2$ and $^{12}$C$^{18}$O$^{16}$O in industrial grade CO$_2$ gas purchased from AIRGAS$^{\text{TM}}$. For our analysis we compared three Raman bands from the Q-branch of the $2\nu_2/\nu_1$ Fermi dyad: the lower component, $\nu_-$, of $^{12}$C$^{16}$O$_2$ at $\Delta \nu_V = 1285.4$ cm$^{-1}$, as well
as the upper component, $\nu_+$, for both $^{13}\text{C}^{16}\text{O}_2$ at $\Delta \nu_V = 1370.1 \text{ cm}^{-1}$ and $^{12}\text{C}^{18}\text{O}^{16}\text{O}$ at $\Delta \nu_V = 1365.8 \text{ cm}^{-1}$.

Table 4.1. Experimental conditions for the double resonance of each isotopologue along with the measured cavity finesse.

<table>
<thead>
<tr>
<th>Band</th>
<th>$\Delta \nu_V \text{ (cm}^{-1})^a$</th>
<th>$L \text{ (\mu m)}$</th>
<th>$m_p, m_s$</th>
<th>$\lambda_p, \lambda_s \text{ (nm)}^b$</th>
<th>$F_p, F_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_-(^{12}\text{C}^{16}\text{O}_2)$</td>
<td>1285.4</td>
<td>24.0</td>
<td>55, 49</td>
<td>865.97, 974.44</td>
<td>25000, 30000</td>
</tr>
<tr>
<td>$\nu_+(^{13}\text{C}^{16}\text{O}_2)$</td>
<td>1370.1</td>
<td>24.9</td>
<td>58, 51</td>
<td>866.85, 983.68</td>
<td>25000, 30000</td>
</tr>
<tr>
<td>$\nu_+(^{12}\text{C}^{18}\text{O}^{16}\text{O})$</td>
<td>1365.8</td>
<td>26.2</td>
<td>60, 53</td>
<td>869.20, 986.29</td>
<td>25000, 30000</td>
</tr>
</tbody>
</table>

$^a$ Taken from [40]. $^b$ In vacuum.

The experimental setup was similar to what is described in 4.3.1 with three notable exceptions. First, the direct piezo action cavity assembly [Fig. 3.4(b)] was used in this experiment. This design allowed us a large level of flexibility to take measurements at different pressures. Second, due to the added stability of the cavity assembly, the cavity length could be directly locked to the pump laser frequency using a side of fringe locking assisted by thermally induced cavity bistability as described in section F.2. And third, a Ti:sapphire laser with a linewidth of $< 50 \text{ MHz}$ and a tuning step size of $\Delta \lambda \approx .04 \text{ nm}$ acted as the pump. We used the same second reference laser at the Stokes emission wavelength to tune to the double resonance, as was done in the single gas experiment. Finally, after tuning, the cavity length and pump frequency were stepped through the double resonance while analyzing the Raman emission with a grating spectrometer, also like was done in the single gas experiment.

Fig. 4.5(a) displays the double resonances collected for each of the three isotopologues as a function of wave number, with the pump wavelength on the secondary axis, plotted together with a theoretical curve. The experimental data was collected in three separate runs and the final rate was corrected for path efficiency and the quantum efficiency of our detector. The pump power was $\sim 10 \text{ mW}$ incident on the cavity with the amount coupled into the cavity varying for each run– this was our biggest source of error. Three mode number pairs were used: one each for the $\nu_-(^{12}\text{C}^{16}\text{O}_2)$ band, the $\nu_+(^{13}\text{C}^{16}\text{O}_2)$ band and the $\nu_+(^{12}\text{C}^{18}\text{O}^{16}\text{O})$ band. Table 4.1 provides best estimates for the mode numbers.
Figure 4.5. (a) Experimental (points), taken from industrial grade CO₂ gas at 1400 Torr and \( \approx 40 \text{ mW} \) incident power, and theoretical (solid lines) emission rate. The \( \nu_-(^{12}\text{C}^{16}\text{O}_2) \) band corresponds to the scale on the right while the \( \nu_+(^{12}\text{C}^{16}\text{O}_2) \) and \( \nu_+(^{13}\text{C}^{16}\text{O}_2) \) bands correspond to the scale on the left. The inset shows the emission rate for isotopically pure \( ^{13}\text{C}^{16}\text{O}_2 \) at 1300 Torr and 25 mW incident power. (b) Emission from the \( \nu_+(^{13}\text{C}^{16}\text{O}_2) \) band vs. the partial pressure of \( ^{13}\text{C}^{16}\text{O}_2 \). The emission rate is taken from the peak rate of a fit to the data and the error bars are the standard error from the fit parameters.

and cavity lengths, which do not take into account unknown parameters, most notably frequency dependent phase shifts from the mirrors.
Table 4.2. Summary of the relative concentration measured for each isotopologue along with the naturally occurring concentrations, Raman shifts and Raman scattering cross-sections.

<table>
<thead>
<tr>
<th>Band</th>
<th>$\Delta \nu_V$ (cm$^{-1}$)[40]</th>
<th>$\Delta \nu_R$ (GHz) $^a$</th>
<th>$\frac{d\sigma}{d\Omega}$ $^b$</th>
<th>$\eta_{exp}$ $^c$</th>
<th>$\eta_{nat}$ $^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_-(^{12}\text{C}^{16}\text{O}_2)$</td>
<td>1285.4</td>
<td>4.5 (3.9[47])</td>
<td>.89</td>
<td>99.2</td>
<td>98.4</td>
</tr>
<tr>
<td>$\nu_+(^{12}\text{C}^{16}\text{O}_2)$</td>
<td>1388.2</td>
<td>0.3[48]</td>
<td>1.4</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>$\nu_+(^{13}\text{C}^{16}\text{O}_2)$</td>
<td>1370.1</td>
<td>8.7</td>
<td>1.4</td>
<td>0.6</td>
<td>1.1</td>
</tr>
<tr>
<td>$\nu_+(^{12}\text{C}^{18}\text{O}^{16}\text{O})$</td>
<td>1365.8</td>
<td>6.0</td>
<td>1.4</td>
<td>0.1</td>
<td>.4</td>
</tr>
</tbody>
</table>

$^a$ Taken from simulated data,[40] except experimental values were cited $^b$ Relative to the $\nu_1$ band in N$_2$.[49] $^c$ Computed from Eq.(4.10) with data from Fig. 4.10. $^d$ Average naturally occurring abundance.[50]

The theoretical curve was computed as described in the last paragraph in section 4.2.5 and fitted to the data with a scale factor. Then Eq. 4.10 was used to compute the relative concentration from the peak rate, which is displayed for each isotopologue in table 4.2.

Comparison between experimental data and theoretical curves show that isotopic analysis, at widely differing isotopologue concentrations, is complicated by the potential ambiguity of identifying lines close to, or coinciding with, one another, and with significantly differing intensities. This is the case for the $\nu_+(^{13}\text{C}^{16}\text{O}_2)$ band in Fig. 4.5(a) which is seen with a “shoulder” on its blue side. This feature disappears when the test gas is isotopically pure $^{13}\text{C}^{16}\text{O}_2$ [inset of Fig. 4.5(a)]. It results from a single rotational transition ($J = 12$) in the O-branch of the $\nu_+$ band of $^{12}\text{C}^{16}\text{O}_2$ with Raman shift of 1370.05 cm$^{-1}$. Another rotational transition ($J = 14$) from the same branch gives rise to the line at 1366.92 cm$^{-1}$. The Raman shift for these O-branch lines ($\Delta J = -2$) can be computed using the terms tabulated in Ref. [40], which are the same terms used for computing the Q-branch lines ($\Delta J = 0$) above. We have also characterized the concentration dependence of the emission rate for the $\nu_+(^{13}\text{C}^{16}\text{O}_2)$ band, plotted in Fig. 4.5(b), as a function of the $^{13}\text{C}^{16}\text{O}_2$ partial pressure.

4.4.3 Conclusion

In conclusion, we demonstrated Purcell enhanced Raman scattering from a high finesse ($\approx 30,000$) microcavity as a tool for isotopic analysis using only $\sim 10$ mW of laser power.
We were able to resolve the three most common isotopologues of CO\textsubscript{2} gas, which differed in concentration by three orders of magnitude.

### 4.5 Theoretical Analysis

To get a better understanding of how different parameters affect the rate of PERS emission, we computed several plots of $\gamma_{\text{cav}}$ [Eq. 4.10] as a function of $L$. We examined a set of four mirror radii of curvature for two Raman line widths [$\nu_+$ and $\nu_-$ of $^{12}\text{C}^{16}\text{O}_2$ see Table 4.1] at two values (10 000 and 1 000 000) of finesse, which are plotted in Fig. 4.6.

A few things can be taken from Eq. 4.10 and Fig. 4.6. First, reducing the cavity length is advantageous unless $\Delta \nu_R \ll \Delta \nu_c^{(s)}$, i.e., the Raman linewidth is much smaller than the cavity linewidth. This is shown in Fig. 4.6 for $\mathcal{F} = 10 000$ and $\nu_+ (^{12}\text{C}^{16}\text{O}_2)$. This “saturation” of the Purcell effect is the reason it is not manifested in macroscopic cavities.

Second, for the cases where $\Delta \nu_R \gg \Delta \nu_c^{(s)}$, the emission rate is approximately inversely proportional to the Raman linewidth as it dominates the denominator in Eq. 4.10. Third, a reduction in mirror radii of curvature results in an increase in emission rate. And finally, an increase in finesse causes the greatest change in rate compared to the other parameters. In fact, an increase in finesse always results in an increase in rate no matter what the other parameters are.

If we break down the rate enhancement factor of $10^7$ for the PERS rate compared to emission into the same solid angle subtended by the microcavity in free space, we can get a better understanding of the role the different parameters play in Fig 4.6. The dominant cavity effect to the rate enhancement is resonant recirculation, which contributes a factor of $\mathcal{F}/\pi \approx 8000$ [Eq. 3.12]. The second is the enhanced collection, which is calculated as the ratio of the $4\pi$ collection in the cavity to the solid angle used in collection in free space or $4\pi/(\frac{\lambda_s^2}{\pi \omega_0^2}) \approx 170$. And the third is the Purcell factor for Raman scattering $F_p \approx 40$ [Eq. 4.8]. Although the finesse is included in the Purcell factor (through the cavity linewidth), it is directly proportional to the magnitude of resonant recirculation and therefore is the dominate factor determining the rate of PERS, as shown in Fig 4.6.
Figure 4.6. (a) A plot, for two Raman lines, $\nu_+(^{12}\text{C}^{16}\text{O}_2)$ (solid) and $\nu_-(^{12}\text{C}^{16}\text{O}_2)$ (dashed), of emission rate [Eq. (4.10)], at 760 Torr and coupled power of .1 mW, vs. cavity length $L$ for a family of four radii of curvature, 10 $\mu$m (green), 20 $\mu$m (blue), 30 $\mu$m (purple), 40 $\mu$m (red) from top to bottom, at a cavity finesse of $\mathcal{F}=100\,000$. Note that only lengths that are in the region of stability of the cavity, $L<2\text{ROC}$, are plotted. (b) Same as in (a) except $\mathcal{F}=10\,000$.

Furthermore, the radii of curvature of the mirrors determine the mode volume, which is inversely proportional to the Purcell factor. Hence, smaller radii of curvature produce a higher rate, also shown in Fig. 4.6. These two observations combined show why, for PERS, a smaller sample size can be used. A decrease in mode volume has no effect on finesses and therefore no effect on the magnitude of resonate recirculation, but it does increase the Purcell factor and it also concentrates the recirculated light into a smaller space. Unlike in
free space, these effects compensate for the lower signal from less scatterers and therefore
PERS requires a dramatically smaller sample size.

4.6 PERS Conclusion

We have demonstrated PERS by means of a double resonant Fabry-Pérot microcavity
with an enhancement of $10^7$ over scattering into the same conditions in free space. Moving
forward there is room for improvement beyond the obvious doubling the signal by collecting
from both sides of the cavity. With an already attainable [51] increase in finesse of an
order of magnitude and a decrease in pump wavelength, where detector quantum efficiency
is around 20%, detection limits at parts per billion levels could be achievable. This would
put PERS on par with IR absorption techniques with a much smaller sample size and the
ability to work with non-IR active molecules.

In the lab a spectrometer was used, but in general there is no need for an extra device
as the cavity itself functions a spectral selection device. This puts PERS at an advantage
compared to other Raman scattering enhancement schemes by allowing a higher resolution
in a much smaller size and with less separate parts as this could be implemented with
filters.

Furthermore, in the last step out of the laboratory and into a viable product, the
low cost of micromirror fabrication and their small size would allow a PERS device to be
implemented with a small footprint at low cost possibly in a hand held device.
CHAPTER 5
MICROCAVITY ENHANCED COHERENT ANTI-STOKES RAMAN SCATTERING (CARS)

5.1 Introduction

The second experiment in which microcavities were employed was the enhancement of coherent anti-Stokes Raman scattering (CARS) by CO$_2$ gas. CARS is a third order nonlinear process that occurs at the same vibrational frequencies as spontaneous Raman scattering, often with emission orders of magnitude greater than spontaneous Raman scattering [20]. CARS first gained notoriety in gas analysis [52], but has been extend to other fields such as microscopy [53, 54]. Here we obtained a rate of photon emission from CO$_2$ CARS of $\approx 10^7$ photons/s by using resonant recirculation, Eq. (3.12), at the pump and Stokes frequencies.

5.2 Theoretical Discussion

5.2.1 Coherent Anti-Stokes Raman Scattering

CARS is a third order non-linear mixing process. The polarization of a medium can be described as [55]

$$P(\omega) = \varepsilon_0 \chi^{(1)} E(\omega) + \varepsilon_0 \chi^{(2)} E^2(\omega) + \varepsilon_0 \chi^{(3)} E^3(\omega)$$

(5.1)

where $\chi$ is the dielectric susceptibility and $E$ is the applied electric field. The first term, which contains the first order susceptibility, is responsible for classical first order linear optics such as the linear optical property of an index of refraction. The next two terms, which contain the second and third susceptibilities, only become important when field strengths
approach very high levels. Here we are concerned only with $\chi^{(3)}$, which is responsible for CARS.

Degenerate CARS occurs when two waves of frequency $\omega_p$ combine with one wave of frequency $\omega_s$ inside a medium with a third order nonlinear susceptibility, $\chi^{(3)}_{\text{CARS}}$, to produce a fourth wave at frequency $\omega_{as}$, where the subscripts stand for pump, Stokes, and anti-Stokes. A CARS energy diagram is shown in Fig. 5.3(b).

### 5.2.1.1 CARS Momentum Matching

The relationship between the intensity of the anti-Stokes signal, $I_{as}$, and the Stokes and Pump electric fields, $E_s$ and $E_p$, is

$$I_{as} = \frac{\omega_{as}^2}{8\varepsilon_0 c} |\varepsilon_0| \frac{3}{4} \chi^{(3)}_{\text{CARS}} E_p^2 E_s^* |L|^2 \text{sinc}^2(\Delta k L/2).$$

(5.2)

The details of Eq. 5.2 can be found in appendix D. Eq. 5.2 shows the intensity of the signal directly depends on the term $\text{sinc}^2(\Delta k L/2)$. The $\Delta k$ is known as the momentum matching condition and is equal to

$$\Delta k = 2k_p - k_s - k_{as}$$

(5.3)

where $k_i$ is the wave vector for each of the four waves.

![Figure 5.1. Wave vector representation of the CARS momentum matching condition.](image-url)
The momentum matching condition is a direct result of the fact that propagating waves move in and out of phase because of the dispersion of the medium.

To take care of the phase matching in free space, the pump and Stokes beams are crossed at an angle $\theta$ and the CARS beam emerges at an angle $\theta'$ as depicted in Fig. 5.1. Perfect phase matching occurs when $\Delta k = 0$ and drops off when there is deviation from this ideal condition as shown in Fig. 5.2.

![Figure 5.2. Efficiency of momentum matching for CARS.](image)

5.2.2 Mirocavity CARS

Ideally, we would create a triple resonance, but frequency dependent phase shifts from the mirrors prevent this in our current setup. Furthermore, the high reflectivity bandwidth of our cavity’s mirrors is smaller than the frequency spanned by the Stokes and the anti-Stokes (i.e. two times the Raman shift) for CO$_2$ gas. This lead to a compromise, where the cavity was tuned to a double resonance for the pump and Stokes, while the anti-Stokes was left in a low reflectivity region outside the high reflectivity bandwidth as shown in Fig. 5.3 (a). Although this reduces the effect that the cavity has on emission, namely the Purcell effect, the wider linewidth, at the low reflectivity region allows for the anti-Stokes to still be within the cavity resonance with out being exactly on resonance. This allows
us to satisfy the phase matching condition for the wave vectors, $k_{as} = 2k_p - k_s$. In free space this takes precise geometry, but inside a cavity this can be achieved by matching to longitudinal modes.

$$\omega_p = \omega_s + \omega_a$$

Figure 5.3. (a) The Three CARS wavelengths on a theoretical plot (black line) of the mirror reflectivity with measured reflectivity (black dots). (b) CARS energy diagram.

The field within a cavity, for each mode $j$, is defined by

$$E_j(r, t) = \sqrt{\frac{\hbar \omega_j}{\varepsilon_0 V_j}} a_j(t) e^{-i\omega_j t} u_j(r)$$

(5.4)

where $\hbar$ is Planck’s constant, $\omega_j$ is the wave’s frequency, $\varepsilon_0$ is the vacuum permittivity, $a_j(t)$ is the slowly time varying amplitude and $u_j(r)$ is the spatial mode function. The spatial mode functions are determined by the type of cavity with the normalization factor, $V_j$, given by

$$V_j = \frac{1}{2} \int u_j^* u_j d^3r.$$  

(5.5)

This means that $|a_j|^2$ represents the energy stored in each mode, in units of $\hbar \omega_j$, which is equal to the number of photons $n_j = |a_j|^2$. This is for all three modes within the cavity: pump, Stokes and anti-Stokes ($p, s, as$).
With this we can describe the dynamics of CARS within a cavity by starting with Maxwell’s equations \([56, 57]\), for each mode, and simplify by assuming all fields are polarized in the same direction

\[
-\nabla^2 E_j + \frac{1}{c^2} \frac{\partial^2 E_j}{\partial t^2} = -\frac{1}{\varepsilon_0 c^2} \frac{\partial^2 P_{NL}^{(3)}(\omega_j)}{\partial t^2}
\]

(5.6)

where for degenerate CARS \(P_{NL}^{(3)}(\omega_{as}) = \varepsilon_0 \frac{3\chi_{CARS}^{(3)}}{4} E_p^2 E_s^*\) [55].

By inserting Eq. (5.4) for \(j=as\) into Eq. (5.6) we get

\[
-\sqrt{\hbar \omega_{as}} \varepsilon_0 V_{as} a_{as}(t)e^{-i\omega_{st}c^2 \nabla^2 u_{as}(r)} + \sqrt{\hbar \omega_{as}} \frac{\varepsilon_0 V_{as}}{\varepsilon_0 V_p} u_{as}(r)\frac{\partial^2}{\partial t^2} (a_{as}(t)e^{-i\omega_{as}t})
\]

\[
= -\frac{3\chi_{CARS}^{(3)}}{4} \frac{\hbar \omega_p}{\varepsilon_0 V_p} \sqrt{\omega_p \omega_s \omega_{as}} \frac{\varepsilon_0 V_{as}}{\varepsilon_0 V_s} u_p(r)^2 u_s(r)^* \frac{\partial^2}{\partial t^2} (a_p(t)^2 a_s(t)^* e^{-i(2\omega_p - \omega_s)t}).
\]

(5.7)

Using the slowly varying envelope approximation, solving for the term \(u_{as}(r)\frac{da_{as}}{dt}\), and then multiplying both sides by \(\frac{1}{2} u_{as}(r)^*\) and integrating, we end up with the anti-Stokes photon rate equation

\[
\frac{da_{as}(t)}{dt} = i \frac{3\chi_{CARS}^{(3)} \hbar \omega_p \sqrt{\omega_p \omega_s \omega_{as}}}{{\varepsilon_0 V_{eff} \varepsilon_0 V_p}} a_p(t)^2 a_s(t)^*
\]

(5.8)

where the effective mode volume is defined by

\[
V_{eff} = \frac{1 \int u_{as}^* u_{ps}^* u_{as} d^3r}{\left( \int u_{ps}^* u_{ps} d^3r \right) \left( \int u_{as}^* u_{as} d^3r \right)^{1/2} \left( \int u_{as}^* u_{as} d^3r \right)^{1/2}}.
\]

(5.9)

The calculation for the CARS effective mode volume can be found in appendix B.3 and is given by

\[
V_{eff} \approx \frac{\lambda_p \sqrt{\lambda_{as} \lambda_s} \left( \frac{2}{\lambda_p} + \frac{1}{\lambda_s} + \frac{1}{\lambda_{as}} \right) L^2}{\tan^{-1} \left( \frac{L}{\sqrt{2L(R - \frac{L}{2})}} \right)}.
\]

(5.10)

Due to the small cavity length, \(\approx 20\mu m\), the differences in the index of refraction for the three wavelengths could be neglected. To get the rate of anti-Stokes photons exiting the
cavity we can start with Eq. (5.8) and subtract from the left side a term to account for
decay due to transmission through the mirrors, which gives

\[
\frac{da_{as}(t)}{dt} = \frac{3\chi^{(3)}_{CARS}}{4} \frac{\hbar \omega_p \sqrt{\omega_s \sqrt{\omega_{as}}}}{\varepsilon_0 V_{eff}} a_p(t) a_s(t) - \frac{a_{as}(t)}{2\tau_c^{as}(t)}. \quad (5.11)
\]

Next we evaluate Eq. (5.11) under steady state conditions and use the relation
\[n_{as} = |a_{as}|^2\]
to get the number of anti-Stokes photons in the mode

\[
n_{as} = (\tau_c^{as})^2 \frac{3\chi^{(3)}_{CARS}}{4} \frac{\hbar^2 \omega_p^2 \omega_s \omega_{as}}{\varepsilon_0^2 V_{eff}^2} n_{p}^2 n_{s}. \quad (5.12)
\]

From here we can get the rate by using the Stokes’ photon cavity lifetime, \(\gamma_{CARS} = n_{as}/2\tau_c^{as}\), which gives

\[
\gamma_{CARS} = \frac{3\chi^{(3)}_{CARS}}{8\Delta \omega_c^{as}} \frac{\hbar^2 \omega_p^2 \omega_s \omega_{as}}{\varepsilon_0^2 V_{eff}^2} n_{p}^2 n_{s}, \quad (5.13)
\]

with the cavity linewidth at the anti-Stokes frequency given by \(\Delta \omega_c^{as}\). The third order
susceptibility, \(\chi^{(3)}_{CARS}\), can be related to measurable quantities by [58]

\[
|\chi^{(3)}_{CARS,0}| = \frac{8\pi^2 \varepsilon_0 N c^4}{\hbar \omega_s^3 \omega_p \Delta \omega_R} \left(\frac{d\sigma}{d\Omega}\right), \quad (5.14)
\]

where \(N\) is the number of molecules in the lower rovibrational state, \(d\sigma/d\Omega\) is the scattering
cross section, and \(\Delta \omega_R\) is the Raman linewidth. If we plug Eq. (5.14) into Eq. (5.13) and
account for the overlap of the Raman and cavity lineshapes by approximating both by
Lorentzian profiles and integrating over frequency, we get the rate of photons exiting one
side of the cavity as

\[
\gamma_{CARS} = \frac{1}{2} \left(\frac{c^4}{2(2\pi)^3}\right) \frac{\lambda_s^5 N^2}{\lambda_0 V_{eff}^2} \left(\frac{d\sigma}{d\Omega}\right)^2 \frac{n_p^2 n_s}{(\Delta \nu_c^{(as)} + \Delta \nu_R^2) \Delta \nu_R^2}. \quad (5.15)
\]

To use this equation we can relate the measurable laser power to photon number within
the cavity by \(n_{p,s} = 2P_{p,s} \tau_c^{(p,s)}/\hbar \omega_{p,s}\), where \(\tau_c^{(p,s)} = 1/\Delta \nu_c^{(p,s)}\) is the relation between inner
cavity photon lifetime and the cavity linewidth.

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5.3 Experimental

For this experiment we used the same cavity and housing that was described in the previous experiment with PERS of CO\textsubscript{2} gas, which is shown in Fig. 3.4(a). In this experiment though, we did not lock the cavity length to the pump laser’s frequency and measure the emission while tuning the laser through the Raman line. We continuously scanned the pump’s frequency and the cavity length through the Raman line, during which, the Stokes’ laser frequency was held constant. The pump frequency and the cavity length were scanned at rates separated by several orders of magnitude (the pump frequency was scanned over 2.4 GHz with a period of 11 seconds and the cavity length was swept through a relative length of 1.42 nm in 3.2 milliseconds), this way all possible frequency and length combinations could be realized. The Stokes laser’s frequency could then be stepped through the resonance while the cavity and pump were scanned. The anti-Stokes emission was separated with a dichroic mirror and detected with a single photon counting module. Fig. 5.4 displays the scanning and filtering setup.

![Experimental setup with dichroic mirror (dashed line) for isolating the CARS emission.](image)

Like in the PERS experiment we used the $\nu_+$ band of the $2\nu_2/\nu_1$ Fermi dyad of the Q-branch of CO\textsubscript{2} at $\Delta \nu = 1388.17$ cm$^{-1}$. Since our cavity was the same, we also used the same longitudinal modes, cavity length, and frequencies as before with the laser at the
Stokes frequency used for tuning and also the Stokes wave in the CARS four wave mixing process.

For 100% CO$_2$ at atmospheric pressure, the full resonance was mapped out in Fig. 5.5(b). As noted in the preceding paragraph, the pump frequency and cavity length were continuously scanned while the Stokes laser’s frequency was stepped through, which produces a near Lorentzian line shape for each Stokes frequency. The plots, and all data, have been corrected for filter losses (50%) and detector quantum efficiency (65%). Fig. 5.5(a) shows the spectrum at the Stokes laser frequency where the peak emission occurs. The peak rate in this plot was compared to Eq. (5.15), with $L \approx 20\mu$m, $F^{(p,s)} \approx 10000$, $F^{as} \approx 3$, $P_p \approx 0.7\text{mW}$ and $P_s \approx 3\text{mW}$, which gave a theoretical value of approximately $1 \times 10^7$ photons/s– within an order of magnitude of the measured rate.

Figure 5.5. (a) A trace for the Stokes frequency at which the maximum occurs. (b) The full CARS spectra where the pump laser was swept over the resonance while the Stokes laser was stepped through a series of frequencies.

We further compared our theoretical description to experimental data. In fig. 5.6 (a) the emission vs. concentration of CO$_2$ in air is plotted. The expected dependence on $N^2$ is not shown; the plot is linear. This is due to the linewidth’s dependence on concentration, shown in Fig. 5.6 (b). The linewidth reduction is attributed to collisional narrowing [47], which our data shows is stronger for air than CO$_2$ i.e. the higher percentage of air the lower the linewidth. To regain the quadratic dependence, the emission rate was divided by the linewidth and plotted versus percent CO$_2$ in fig 5.6 (c). In fig. 5.6 (d) the input power
of both the pump and Stokes lasers versus the CARS emission rate was plotted and they both approximately agree with Eq. 5.15.

![Graphs](image)

Figure 5.6. (a) Peak CARS emission rate versus CO$_2$ concentration. (b) Raman linewidth versus CO$_2$ concentration. (c) Logarithmic plot of emission rate in (a) multiplied by the line width in (b) squared [see Eq. (5.15)] to show quadratic dependence. (d) Dependence of the microcavity CARS emission rate on pump and Stokes laser power.

We can get a better understanding of the cavity’s enhancement effect from a comparison to CARS in free space with the same amount of gas. We get the intensity of Stokes radiation from the CARS process starting with Eq. D.3

$$I_{as} = \frac{\omega_{as}}{8\varepsilon_0 c} |P_{CARS}^{(3)}|^2 \text{sinc}^2(\Delta kL/2),$$

where the (complex) nonlinear polarization is $P_{CARS}^{(3)} = \varepsilon_0 \frac{3\chi_{CARS}^{(3)}}{4} E_p^2 E_s^*$, the interaction length is $L$ and the wavevector phase matching condition is $\Delta k = 2k_p - k_s - k_{as}$. We can assume an interaction length of one Rayleigh range, $L = \pi w_p^2/\lambda_p$, with a cross sectional
area of $\pi w_0^2$, which gives, at perfect phase matching conditions ($\Delta k = 0$), the power of anti-Stokes radiation as

$$P_{as} = \left(\frac{\lambda_s^3}{2hc\lambda_{as}}\right)^2 \left[\frac{N}{\Delta\omega_R} \frac{d\sigma}{d\Omega}\right] P_p^2 P_s,$$

where the CARS emission rate can be calculated using $\gamma_{\text{CARS,free}} = P_{as}/h\nu_{as}$. In free space using the same laser powers we obtain $\gamma_{\text{CARS,free}} \approx 6 \times 10^{-4}$ photons/s, which is 9 orders of magnitude less than the cavity value. If instead we use the calculated circulating powers for $P_s$ and $P_p$, we get $\gamma_{\text{CARS,free}} \approx 10^7$ photons/s, which is the same order as the microcavity enhanced results. This demonstrates that the enhancement comes from increased circulating intensity and not the Purcell effect, which makes sense as the anti-Stokes frequency is outside of the high reflectively band of the microcavity, as mentioned earlier.

### 5.4 Conclusion

We have further shown the versatility of our microcavities by demonstrating microcavity enhanced CARS from CO$_2$ gas (1 atm) with a peak rate $\sim 10^6$ photons/s from a microscopic sample volume and milliwatts of pump power. Although our limited bandwidth did not allow for high finesse at the anti-Stokes frequency and frequency dependent phase shifts limited the anti-Stokes frequency to the fringe of a broad resonance, this technique has potential to be used in gas sensing. More importantly it has opened the door for the use of microcavities in non-linear processes. Commercial available dielectric coatings can be made with frequency independent phase shifts (over a finite bandwidth) and this could be used to realize a triple resonance, where all three frequencies lie at the center of a sharp resonance. This could allow for novel applications such as one in which microcavity enhanced CARS is used as a source for correlated photon pairs [59].
CHAPTER 6
SUMMARY AND OUTLOOK

The experiments presented in this dissertation have laid the foundations for the use of high finesse Fabry-Pérot microcavities to enhance Raman scattering from gases. PERS has shown its utility as a method for single gas concentration sensing and also isotopic ratio analysis of gases. Possible future directions for PERS include multi-gas analysis and compact high resolution Raman spectroscopy, where the microcavity is also used as a spectrometer. Furthermore, the micromirror fabrication technique has potential for low cost fabrication of micromirrors in bulk and this, along with the small size of the microcavity, gives PERS the possibility to move out of the laboratory and into consumer products.

Beyond PERS, microcavity enhancement of CARS also has potential future applications that use non-linear processes, such as a possible source for correlated photon pairs and frequency conversion.

Going forward with microcavity enhanced Raman scattering, there are a few notable improvements to be made. First, an order of magnitude increase of the finesse, which is readily obtainable [51], would result in over an order of magnitude increase signal. Second, our experiments suffered from low collection and detection efficiency of the scattered light (≈ 1% overall detection efficiency). The collection efficiency could easily be improved by collecting from both sides of the microcavity (instead of just one side) and by using a system of filters or, as stated in the paragraph above, the cavity itself for spectral selection in place of an inefficient grating spectrometer. Also, detector quantum efficiencies beyond 50% [60] are commercially available and would be an easy improvement to performance. These readily obtainable improvements could put detection limits in the single ppm region.
It is also worth noting that several issues, which had the potential to damage our micromirrors, had a negligible effect. First was exposure to environmental conditions. Our mirrors, over the course of the five year time period in which these experiments were conducted, were directly exposed to the ambient conditions of our lab, which included the high humidity of Florida. Second was the high intensity of light incident on the mirrors. Laser powers incident on the cavity, at times, reached levels of $\approx 50$ mW, which corresponds to a circulating intensity on the mirror surface of $\approx 2 \times 10^8$ W/cm$^2$. Third was the build up of heat due to the high circulating intensity. This well known phenomenon in high finesse micro resonators [61], which is documented in our microcavities in appendix F.2, causes thermal induced changes in the index of refraction of the mirror material. Measurements of the microcavity finesse upon the conclusion of the experiments reveal little loss in mirror reflectivity compared to the measurements taken when the microcavities where first assembled. Furthermore, there was no noticeable reduction in the Raman signal between experiments. This suggests the microcavities would retain a high level of functionality when exposed to similar conditions encountered by a commercial gas sensing system.

This work’s main contribution was to lay the foundation for PERS, but it has also contributed to the general knowledge of high finesse Fabry-Pérot microcavities, which have applications in fields as far reaching as imaging [62] and quantum computing [63, 64, 65]. In the six years since the first high finesse Fabry-Pérot microcavity experiments were performed, the technology has shown great promise and this work has only been a small demonstration of the future possible uses.
REFERENCES


Appendix A Quantization of the Electromagnetic Field

Outlined is a brief description of the quantization of the electromagnetic field adapted from [58].

A.1 Mode Expansion in a 3D Cavity

Start with Maxwell’s equations in a vacuum

\[ \nabla \cdot E = 0 \quad (A.1) \]

\[ \nabla \cdot B = 0 \quad (A.2) \]

\[ \nabla \times E = \mu_0 \epsilon_0 \frac{\partial E}{\partial t} \quad (A.3) \]

\[ \nabla \times B = -\frac{\partial B}{\partial t} \quad (A.4) \]

Imagine a classical electromagnetic field inside a cavity of volume \( V \) bound by a surface \( S \). For a perfectly conducting cavity

\[ \mathbf{n}(r) \times \mathbf{E}(r) = 0 \quad (A.5) \]

\[ \mathbf{n}(r) \cdot \mathbf{B}(r) = 0, \quad (A.6) \]

where \( \mathbf{n}(r) \) is the unit vector normal to \( S \). We can expand \( \mathbf{E} \) and \( \mathbf{B} \) into two orthogonal set of vector fields \( \mathbf{E}_a \) and \( \mathbf{B}_a \) which obey

\[ \nabla \times \mathbf{E}_a(r) = k_a \mathbf{B}_a(r) \quad (A.7) \]

\[ \nabla \times \mathbf{B}_a(r) = k_a \mathbf{E}_a(r). \quad (A.8) \]

By using the identity \( \nabla \times \nabla \times \mathbf{A} = \nabla (\nabla \cdot \mathbf{A}) - \nabla^2 \mathbf{A} \) and taking the curl of both sides of equations (A.7) and (A.8), we get the Helmholtz equations
Appendix A (Continued)

\[ (\nabla^2 + k_a^2) E_a(\mathbf{r}) = 0 \]  \hspace{1cm} (A.9)

\[ (\nabla^2 + k_a^2) B_a(\mathbf{r}) = 0, \]  \hspace{1cm} (A.10)

where \( k_a = \omega_a/c \) and \( \omega_a \) is the cavity resonance frequency of mode \( a \) determined by the geometry of the cavity. \( E_a \) and \( B_a \) form a complete set and they obey the orthonormality conditions

\[ \int_V d^3r \mathbf{E}_a \cdot \mathbf{E}_b = \delta_{ab} \]  \hspace{1cm} (A.11)

\[ \int_V d^3r \mathbf{B}_a \cdot \mathbf{B}_b = \delta_{ab}. \]  \hspace{1cm} (A.12)

A.1.1 Proof of Orthogonality

Start by applying the identity \( \nabla \cdot (\mathbf{A} \times \mathbf{B}) = \mathbf{B} \cdot \nabla \times \mathbf{A} - \mathbf{A} \cdot \nabla \times \mathbf{B} \) to \( (\mathbf{E}_b \times \nabla \times \mathbf{E}_a) \) and \( (\mathbf{E}_a \times \nabla \times \mathbf{E}_b) \) and subtract them from each other

\[ \nabla \times (\mathbf{E}_b \times \nabla \times \mathbf{E}_a) - \nabla \times (\mathbf{E}_a \times \nabla \times \mathbf{E}_b) \]

\[ = \nabla \times \mathbf{E}_a \cdot \nabla \times \mathbf{E}_b - \mathbf{E}_b \cdot \nabla \times \nabla \times \mathbf{E}_a - \nabla \times \mathbf{E}_b \cdot \nabla \times \mathbf{E}_a + \mathbf{E}_a \cdot \nabla \times \nabla \times \mathbf{E}_b. \]

The first and third terms on the second line cancel and by using (A.7) and \( \nabla \times \nabla \times \mathbf{E}_b = k_a^2 E_a^2 \) we get

\[ k_a \nabla \cdot (\mathbf{E}_b \times \mathbf{B}_a) - k_b \nabla \cdot (\mathbf{E}_a \times \mathbf{B}_b) = (k_b^2 - k_a^2) \mathbf{E}_a \cdot \mathbf{E}_b. \]

We can take the integral of both side over a volume \( V \) to get

\[ \int_V k_a \nabla \cdot (\mathbf{E}_b \times \mathbf{B}_a) - k_b \nabla \cdot (\mathbf{E}_a \times \mathbf{B}_b) d^3r = (k_b^2 - k_a^2) \int_V \mathbf{E}_a \cdot \mathbf{E}_b d^3r \]
Appendix A (Continued)

and then apply Gauss's theorem, \( \int_V (\nabla \cdot F) \, dr^3 = \oint (F \cdot n) \, ds \), to the left side to get

\[
\oint k_a n \cdot (E_b \times B_a) - k_b n \cdot (E_a \times B_b) \, dr^3 = (k_b^2 - k_a^2) \int_V E_a \cdot E_b \, dr^3
\]

Next use the triple product identity: \( A \cdot B \times C = C \cdot A \times B \). This leave us with

\[
\oint k_a B_a \cdot (n \times E_b) - k_b B_b \cdot (n \times E_a) \, dr^3 = (k_b^2 - k_a^2) \int_V E_a \cdot E_b \, dr^3
\]

and from (A.5) we see the left side must be zero. Therefore if \( k_b \neq k_a \), then \( \int_V E_a \cdot E_b \, dr^3 \) must be zero.

Since the mode functions are a complete othonormal set and the boundary conditions are independent of time, we can separate time and space and write the electric and magnetic fields and associated vector potential as

\[
E(r, t) = - \sum a \frac{1}{\sqrt{\epsilon_0}} P_a(t) E_a(r)
\]

(A.13)

\[
B(r, t) = \sum a \sqrt{\mu_0 \omega_a} Q_a(t) B_a(r)
\]

(A.14)

\[
A(r, t) = \sum a \frac{1}{\sqrt{\epsilon_0}} Q_a(t) E_a(r),
\]

(A.15)

where \( \omega_a = \frac{k_a}{\sqrt{\omega_0 \epsilon_0}} \). Substituting (A.13) and (A.14) into (A.4) gives

\[
\nabla \times E(r, t) = - \frac{\partial B}{\partial t}
\]

\[
- \nabla \times \sum_a \frac{1}{\sqrt{\epsilon_0}} P_a(t) E_a(r) = - \sum_a \frac{\partial \sqrt{\mu_0 \omega_a} Q_a(t) B_a(r)}{\partial t}.
\]

We can then solve for one of the series of differential equations
Appendix A (Continued)

\[
\frac{1}{\sqrt{\varepsilon_0}} P_a(t) \nabla \times E_a(r) = \sqrt{\mu_0 \omega_a} B_a(r) \frac{\partial Q_a(t)}{\partial t}.
\]

Then using (A.7) and \( \omega_a = \frac{k_a}{\sqrt{\omega_0 \varepsilon_0}} \) we get

\[
P_a(t) = Q_a(t).
\]

Next, substituting (A.14) and (A.13) into (A.3) gives

\[
\nabla \times B = \mu_0 \varepsilon_0 \frac{\partial E}{\partial t}
\]

\[
\nabla \times \sum_a \sqrt{\mu_0 \omega_a} Q_a(t) B_a(r) = -\mu_0 \varepsilon_0 \sum_a \frac{1}{\sqrt{\varepsilon_0}} \frac{\partial P_a(t)}{\partial t} E_a(r) \partial t.
\]

We can then solve for one of the series of differential equations

\[
\sqrt{\mu_0 \omega_a} Q_a(t) \nabla \times B_a(r) = -\mu_0 \varepsilon_0 \frac{1}{\sqrt{\varepsilon_0}} E_a(r) \frac{\partial P_a(t)}{\partial t}.
\]

Then using (A.8) and \( \omega_a = \frac{k_a}{\sqrt{\omega_0 \varepsilon_0}} \) we get

\[
\sqrt{\mu_0 \omega_a} Q_a(t) \frac{\omega_a}{c} E_a(r) = -\mu_0 \varepsilon_0 \frac{1}{\sqrt{\varepsilon_0}} E_a(r) \frac{\partial P_a(t)}{\partial t}
\]

\[
P_a(t) = Q_a(t).
\]

This leaves us with an infinite set of differential equations

\[
P_a(t) = Q_a(t) \quad (A.16)
\]

\[
P_a(t) = -\omega_a^2 Q_a(t). \quad (A.17)
\]
Appendix A (Continued)

A.2 Quantization of the Radiation Field

The total energy Hamiltonian is

\[ H = \frac{1}{2} \int_V (\epsilon_0 E^2 + \frac{1}{\mu_0} B^2) dv. \]  \hspace{1cm} (A.18)

We can substitute (A.13) and (A.14) into (A.18) and get

\[ H = \frac{1}{2} \int_V \left( \epsilon_0 \left( \sum_a \sqrt{\epsilon_0} P_a(t) E_a(r) \right)^2 + \frac{1}{\mu_0} \left( \sum_a \sqrt{\mu_0 \omega_a} Q_a(t) \right)^2 \right) dv \]

\[ = \frac{1}{2} \sum_a \left( P_a(t)^2 \int_V E_a(r)^2 dv + Q_a(t)^2 \omega_a^2 \int_V B_a(r)^2 dv \right) \]

\[ = \sum_a \frac{1}{2} (P_a(t)^2 + \omega_a^2 Q_a(t)^2). \]

The last equation

\[ H = \sum_a \frac{1}{2} (P_a(t)^2 + \omega_a^2 Q_a(t)^2) \]  \hspace{1cm} (A.19)

has the Hamiltonian of a sum of quantum harmonic oscillators with unit mass, frequency \( \omega_a \), coordinate \( Q_a(t) \) and momentum \( P_a(t) \) for each \( a \). The variables \( P_a(t) \) and \( Q_a(t) \) constitute canonically conjugate variables.

As with the harmonic oscillator, \( P_a \) and \( Q_a \) obey the commuter relations

\[ [P_a, P_b] = [Q_a, Q_b] = 0 \]  \hspace{1cm} (A.20)

\[ [Q_a, P_a] = i \hbar \delta_{a,b}. \]  \hspace{1cm} (A.21)

We can then define raising and lowering operators, as was done with the quantum harmonic oscillator,

\[ a_l^+(t) = \left( \frac{1}{2 \hbar \omega_l} \right)^{\frac{1}{2}} [\omega_l Q_l(t) - i P_l(t)] \]  \hspace{1cm} (A.22)
Appendix A (Continued)

\[ a_l(t) = \left( \frac{1}{2\hbar \omega_l} \right)^\frac{1}{2} [\omega_l Q_l(t) + iP_l(t)], \quad (A.23) \]

with commutator relations

\[ [a_l, a_m] = [a_l^+, a_m^+] = 0, \quad (A.24) \]
\[ [a_l, a_m^+] = \delta_{l,m}. \quad (A.25) \]

Solving (A.22) and (A.23) for \( P_l \) and \( Q_l \) gives

\[ P_l = i (\frac{\hbar \omega_l}{2})^\frac{1}{2} [a_l^+ - a_l] \quad (A.26) \]
\[ Q_l = (\frac{\hbar}{2\omega_l})^\frac{1}{2} [a_l^+ + a_l]. \quad (A.27) \]

The Hamiltonian can also be expressed in terms of the raising and lowering operators as

\[ \mathcal{H} = \sum_l \hbar \omega_l (a_l^+ a_l + \frac{1}{2}). \quad (A.28) \]

A stationary state of the total radiation field can be characterized by an eigenfunction

\[ \Phi = u_{n_1} u_{n_2} \cdots = \Pi_{l=1}^\infty u_{n_l}, \quad (A.29) \]
Appendix A (Continued)

where

\[ a_l^+ u_{nl} = \sqrt{n_l + 1} u_{nl+1} \quad (A.30) \]

\[ a_l u_{nl} = \sqrt{n_l} u_{nl-1} \quad (A.31) \]

\[ a_l^+ a_l u_{nl} = n_l u_{nl} \quad (A.32) \]

and

\[ \langle \Phi | a_l^+ a_l | \Phi \rangle = \langle n_l | a_l^+ a_l | n_l \rangle = n_l, \quad (A.33) \]

which is the number of quanta \( n_l \) in the \( l \)th mode of the resonator.

A.3 Plane-Wave Quantization

Consider the \( l \)th mode of a resonator along the \( z \) axis with a length \( L \) and a mode volume \( V \). Set the electric and magnetic field vectors to point along the \( y \) and \( x \) directions. The conditions set by (A.7), (A.8), (A.11) and (A.12) can be satisfied by choosing

\[ E_l(r) = j \sqrt{\frac{2}{V}} \sin(k_l z) \quad (A.34) \]

\[ B_l(r) = -i \sqrt{\frac{2}{V}} \cos(k_l z), \quad (A.35) \]

where \( k_l = l\pi/L \) and \( l = \text{integer} \).

The corresponding mode fields are

\[ E_{ly}(r, t) = -\sqrt{\frac{2}{V\epsilon_0}} P_l(t) \sin(k_l z) \quad (A.36) \]
Appendix A (Continued)

\[ B_{ly}(r, t) = \omega t \sqrt{\frac{2\mu_0}{V}} Q_l(t) \cos(k_l z) \quad (A.37) \]

and using (A.22) and (A.23) gives

\[ E_{ly}(r, t) = -i \sqrt{\frac{\hbar \omega}{V \epsilon_0}} [a_l^+ - a_l] \sin(k_l z) \quad (A.38) \]

\[ B_{ly}(r, t) = -\sqrt{\frac{\hbar \omega \mu_0}{V}} [a_l^+ + a_l] \cos(k_l z). \quad (A.39) \]
Appendix B Supporting Calculations

B.1 PERS Effective Mode Volume

Outlined is the calculation of $V_{\text{eff}}$ for PERS. Using the spatial mode functions, $u(r)$, with the subscript $p$ for pump laser and $s$ for Stokes, the Purcell factor mode volume is given by [39]

$$V_{\text{eff}} = \frac{\int |u(r)_s|^2 d^3r \int |u(r)_p|^2 d^3r}{\int |u(r)_s|^2 |u(r)_p|^2 d^3r}.$$  \hspace{1cm} (B.1)

For a confined Gaussian beam using Eq. (3.5) we get

$$u(r) = \left[\frac{w_0}{w(z)}\right] \sin(kz)e^{-r^2/w(z)},$$  \hspace{1cm} (B.2)

where $k = 2\pi/\lambda$ is the wave number, the beam spot size, $w(z)$, is given by Eq (3.7), which is determined by the beam waist, $w_0$, and the radii of curvature of the the mirrors.

We begin with a planar concave resonator with $R = L(1 + \frac{z^2}{R^2}/L^2)$ and $z_R^2 = L(R - L)$. For the numerator of Eq. (B.1) we can use polar coordinates

$$\int |u(r)|d^3r = w_0 \int_0^L \int_0^\infty e^{-2r^2/w(z)^2} - \frac{2\pi r dr \sin^2(kz) dz}. \hspace{1cm} (B.3)$$

Now using $\int xe^{-ax^2}dx = \frac{-1}{2a} e^{-ax^2}$ we get

$$\int |u(r)|d^3r = \frac{\pi w_0^2}{2} \int_0^L \sin^2(kz) dz = \frac{\pi w_0^2 L}{4}. \hspace{1cm} (B.4)$$

Next we can move to the denominator of Eq. (B.1) which is given by
Appendix B (Continued)

\[
\int |u(r)_s|^2|u(r)_p|^2d^3r = w_0^2 w_0^2 \int_0^L \int_0^\infty \frac{e^{-r^2[w_p(z)^{-2}+w_s(z)^{-2}]}}{w_p(z)w_s(z)} 2\pi rd_3r \tag{B.5}
\]

\[
\times \sin^2(k_p z)^2 \sin^2(k_s z)dz
\]

and using the relation \(w_s(z)^2 = w_p(z)^2 \lambda_s / \lambda_l\), we get

\[
\int |u(r)_s|^2|u(r)_p|^2d^3r = w_0^2 w_0^2 \frac{\pi/2}{1 + \lambda_s / \lambda_p} \int_0^L \frac{\sin^2(k_p z)^2 \sin^2(k_s z)}{w_p(z)^2} dz. \tag{B.6}
\]

The \(z\) integral can be approximated by assuming the \(w_p(z)^{-2}\) term varies slowly compared to the harmonic terms and treating them as two separate integrals. Using trigonometric identities we have \(\int_0^L \sin^2(k_p z)^2 \sin^2(k_s z)dz = 1/4\) which can be plugged into Eq. (B.6) to get

\[
\int |u(r)_s|^2|u(r)_p|^2d^3r = w_0^2 w_0^2 \frac{\pi/8}{1 + \lambda_s / \lambda_p} \int_0^L w_p(z)^{-2}dz. \tag{B.7}
\]

If we substitute Eq. (3.7) in for \(w_p(z)\) and using \(\int \frac{1}{1+x^2}dx = \tan^{-1}(x)\) we get

\[
\int |u(r)_s|^2|u(r)_p|^2d^3r = w_0^2 w_0^2 \frac{\pi/8}{1 + \lambda_s / \lambda_p} \sqrt{L(R-L)} \tan^{-1} \frac{L}{\sqrt{L(R-L)}}, \tag{B.8}
\]

where we made use of the \(Z_{2R}^2 = L(R-L)\) for planar concave cavities. If we plug in Eq. (B.4), for both \(p\) and \(s\), and Eq. (B.8) into Eq. (B.1), we get

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Appendix B (Continued)

\[ V_{\text{eff}} = \frac{(\lambda_p + \lambda_s)L^2/2}{\tan^{-1} \frac{L}{\sqrt{L(R-L)}}}, \]  

which can be generalized for a symmetric cavity of length \( L \) as

\[ V_{\text{eff}} = (\lambda_p + \lambda_s) \frac{L^2/4}{\tan^{-1} \frac{L}{\sqrt{2(R-L/2)L}}} . \]  

(B.10)

B.2 PERS Double Resonance Line Shape

Since the cavity length is locked to the pump frequency and both are scanned over the Raman line, the resulting double resonance is a convolution of the two line shapes. The cavity has a longitudinal mode of \( m_s \) at frequency \( \nu_p - (m_p - m_s) \text{FSR} \), which is modeled as a Lorentzian with a linewidth of \( \Delta \nu_{c(s)} \), where \( \text{FSR} \) is the free spectral range Eq. (3.2). The second, Raman, lineshape is also modeled as a Lorentzian, which is at a frequency of \( \nu_p - \Delta \nu_V \) (\( \Delta \nu_V \) is the Raman shift) with a linewidth of \( \Delta \nu_R \). This makes the double resonance line shape equal to

\[ \gamma_{\text{cav,DR}}(\nu_p) = \gamma_{\text{cav}} \int_{\infty}^{\infty} \frac{1}{((\nu' - (\nu_p - (m_p - m_s) \text{FSR}))^2 + (\Delta \nu_R/2)^2} \times \frac{1}{((\nu' - (\nu_p - \Delta \nu_V))^2 + (\Delta \nu_c^{(s)}/2)^2}) \ dv', \]  

(B.11)

where \( A \) is a normalization constant with the relation

\[ A \int_{-\infty}^{\infty} \frac{1}{\nu'^2 + (\Delta \nu_R/2)^2} \frac{1}{\nu'^2 + (\Delta \nu_c^{(s)}/2)^2} \ dv' = 1, \]  

(B.12)
which when solved for $A$ is

$$A = \frac{\Delta \nu_c^{(s)} \Delta \nu_R (\Delta \nu_c^{(s)} + \Delta \nu_R)}{8\pi}. \quad \text{(B.13)}$$

Using the approximation for FSR, $FSR \approx c/(2L) = c/(2m_p\lambda_p/2) = \nu_p/m_p$, where $c$ is the speed of light, $L$ is the cavity length, and $\lambda_p$ is the pump laser’s wavelength, we get

$$\gamma_{cav,DR}(\nu_p) = \gamma_{cav} A \int_{\infty}^{\infty} \frac{\gamma_{cav} A}{(\nu' - (m_p - m_s)\nu_p/m_p + \Delta \nu_V)^2 + (\Delta \nu_R/2)^2} \times \frac{1}{\nu'^2 + (\Delta \nu_c^{(s)}/2)^2} d\nu', \quad \text{(B.14)}$$

which leads to

$$\gamma_{cav,DR}(\nu_p) = \frac{2\pi\gamma_{cav} A (1/\Delta \nu_c^{(s)} + 1/\Delta \nu_R)}{(m_p - m_s)\nu_p/m_p - \Delta \nu_V)^2 + (\Delta \nu_c^{(s)}/2 + \Delta \nu_R/2)^2} \quad \text{(B.15)}$$

$$= \frac{(1/4)(\Delta \nu_c^{(s)} + \Delta \nu_R)^2 m^2 \gamma_{cav}/(m_p - m_s)^2}{(\nu_p - m_p\Delta \nu_V/(m_p - m_s))^2 + (m_p(\Delta \nu_c^{(s)} + \Delta \nu_R)/(m_p - m_s))^2},$$

which is a Lorentzian of width

$$\gamma_{cav,DR}(\nu_p) = m_p(\Delta \nu_c^{(s)} + \Delta \nu_R)/(m_p - m_s) \quad \text{(B.16)}$$

$$= \frac{\nu_p}{\Delta \nu_V}(\Delta \nu_R + \Delta \nu_c^{(s)}).$$
Appendix B (Continued)

B.3 CARS Effective Mode Volume

Outlined is the calculation of $V_{\text{eff}}$ for microcavity enhanced CARS, which is given by the relation

$$\frac{1}{V_{\text{eff}}} = \frac{1}{V_p V_s V_{as}} \left| \iiint u(r)_{as}^* u(r)_p^2 u(r)_s d^3r \right|. \tag{B.17}$$

Starting with the integral and substituting in the formula for a confined Gaussian beam,

$$u(r) = \left[ w_0/w(z) \right] \sin(kz)e^{-r^2/w(z)} \tag{36},$$

we have

$$\iiint u(r)_{as}^* u(r)_p^2 u(r)_s d^3r = w_0 w_0^2 w_0 \int_0^L \int_0^\infty e^{-r^2[2w_p(z)^{-2} - w_{as}(z)^{-2} - w_s(z)^{-2}]} \frac{w_p(z)w_{as}(z)w_s(z)}{w_p(z)w_{as}(z)w_s(z)} \times \sin(k_p z)^2 \sin(k_{as} z) \sin(k_s z) 2\pi r dr dz. \tag{B.18}$$

The different beams’ spot sizes can all be put in terms of the pump wavelength using

$$w_a(z)^2 = \left[ \lambda_a/\lambda_b \right] w_b(z)^2 \tag{36},$$

which gives

$$\iiint u(r)_{as}^* u(r)_p^2 u(r)_s d^3r = 2\pi w_0^4 \int_0^L \int_0^\infty e^{-r^2[2 + \lambda_p/\lambda_s^2 + \lambda_p/\lambda_{as}^2]w_p(z)^{-2}} \frac{w_p(z)}{w_p(z)} \sin(k_p z)^2 \sin(k_{as} z) \sin(k_s z) r dr dz. \tag{B.19}$$

We can now take the radial integral using $\int_0^\infty e^{-ar^2} dr = \frac{1}{2a}$, where $a = [2 + \lambda_p/\lambda_s + \lambda_p/\lambda_{as}]w_p(z)^{-2}$. This gives
Appendix B (Continued)

\[ \iiint u(r)_{as}^* u(r)_{p}^2 u(r)_{s}^* d^3r \]

\[ = \frac{\pi w_0^4}{(2 + \frac{\lambda_p}{\lambda_s} + \frac{\lambda_p}{\lambda_{as}})} \int_0^L w_p(z)^{-2} \sin(k_p z)^2 \sin(k_{as} z) \sin(k_s z) dz. \]  

(B.20)

Using trigonometry identities and \(2k_p - k_s - k_{as} = 0\), we find that

\[ \sin(k_p z)^2 \sin(k_{as} z) \sin(k_s z) \]

\[ = \frac{1}{8} + \frac{1}{4} \cos((k_s - k_{as}) z) - \frac{1}{4} \cos((k_s + k_{as}) z) - \frac{1}{8} \cos((2k_p - k_s - k_{as}) z) + \frac{1}{8} \cos((2k_p + k_s - k_{as}) z) + \frac{1}{8} \cos((2k_p + k_s + k_{as}) z), \]

and, over the integral, the periodic terms average to zero, so we are left with

\[ \iiint u(r)_{as}^* u(r)_{p}^2 u(r)_{s}^* d^3r \approx \frac{\pi w_0^4}{(2 + \frac{\lambda_p}{\lambda_s} + \frac{\lambda_p}{\lambda_{as}})} \int_0^L w_p(z)^{-2} dz. \]  

(B.21)

We can now use \(w(z)^2 = w_0^2(1 + \frac{z^2}{z_R^2})\), where \(z_R\) is the Rayleigh range. This gives us

\[ \iiint u(r)_{as}^* u(r)_{p}^2 u(r)_{s}^* d^3r \approx \frac{\pi w_0^4}{(2 + \frac{\lambda_p}{\lambda_s} + \frac{\lambda_p}{\lambda_{as}})} \int_0^L \frac{z_R^2}{z_R + z^2} dz. \]  

(B.22)

The integral \(\int \frac{1}{a^2 + x^2} dx = \frac{1}{a} \tan^{-1}\left(\frac{x}{a}\right)\) can be used to give us

\[ \iiint u(r)_{as}^* u(r)_{p}^2 u(r)_{s}^* d^3r \approx \frac{\pi w_0^4}{(2 + \frac{\lambda_p}{\lambda_s} + \frac{\lambda_p}{\lambda_{as}})} z_R \tan^{-1}\left(\frac{L}{z_R}\right). \]  

(B.23)

Then we can substitute \(z_R^2 = L(R - L)\), where \(R\) is the radius of curvature of the mirrors, into the expression to get the final expression for the integral

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Appendix B (Continued)

\[ \int \int \int u(r)_{as}^* u(r)^2 \rho u(r)^* d^3r \approx \frac{w_0^2}{\pi} \left( 2 + \frac{\lambda_p}{\lambda_s} + \frac{\lambda_p}{\lambda_{as}} \right) \sqrt{L(R-L)} \tan^{-1}\left( \frac{L}{\sqrt{L(R-L)}} \right). \]  \hfill (B.24)

Using \( \int |u(r)|^2 d^3r = \pi w_0^2 L^4 \) and \( w_a(z)^2 = [\lambda_a/\lambda_b] w_b(z)^2 \) [36] in (B.17) we get

\[ \frac{1}{V_{eff}} = \frac{1}{\pi^2 L^4 w_0^2 \lambda_{as}\lambda_s/\lambda_p^2} \left( \int \int \int u(r)_{as}^* u(r)^2 \rho u(r)^* d^3r \right). \]  \hfill (B.25)

We can then insert (B.24) into this expression and use \( w_0 = \frac{\sqrt{2}}{\pi} \sqrt{L(L-R)} \) to get

\[ V_{eff} \approx \frac{\lambda_p \sqrt{\lambda_{as}\lambda_s} \left( \frac{2}{\lambda_p} + \frac{1}{\lambda_s} + \frac{1}{\lambda_{as}} \right) L^2}{\tan^{-1}\left( \frac{L}{\sqrt{L(R-L)}} \right)} \]  \hfill (B.26)

and for an arbitrary symmetric resonator we get

\[ V_{eff} \approx \frac{\lambda_p \sqrt{\lambda_{as}\lambda_s} \left( \frac{2}{\lambda_p} + \frac{1}{\lambda_s} + \frac{1}{\lambda_{as}} \right) L^2}{\tan^{-1}\left( \frac{L}{\sqrt{2L(R-L)}} \right) \frac{1}{2}} \]  \hfill (B.27)
Appendix C Quantum Mechanical Description of Spontaneous Raman Scattering

This was adapted from [58]. For an electronic configuration, the potential energy of a molecule is a function of the normal vibration coordinate $X$, where $X = 0$ is the equilibrium point. Transitions between vibrational levels that are induced by a radiation field use the perturbation Hamiltonian

$$\mathcal{H}' = -\mu \cdot \mathbf{E},$$

where $\mu$ is the dipole moment and $\mathbf{E}$ is the electric field; for simplicity I will assume the field vectors all point in the same direction. The dipole moment is made up of two parts. The part induced by an electric field $\mu_i = \varepsilon_0 \alpha E$, where $\alpha$ is the molecular polarizability. The molecular polarizability is a function of $X$ with a series expansion $\alpha(X) = \alpha_0 + (\frac{\partial \alpha}{\partial X})_0 X$, where $(\frac{\partial \alpha}{\partial X})_0$ is the differential polarizability. The second part is the permanent dipole moment, $\mu_p$, with the expansion $\mu^0_p + (\frac{\partial \mu_p}{\partial X})_0 X$. With these terms plugged into (C.1) we get the full Hamiltonian

$$\mathcal{H}' = -[\mu^0_p + (\frac{\partial \mu_p}{\partial X})_0 X \varepsilon_0 \alpha E + \varepsilon_0 (\frac{\partial \alpha}{\partial X})_0 X E],$$

where first and third terms do not cause transitions, as they are independent of $X$, and second term gives rise to infrared absorption, which leaves the last term for Raman scattering. This gives the Raman scattering Hamiltonian as

$$\mathcal{H}' = -\varepsilon_0 (\frac{\partial \alpha}{\partial X})_0 X E^2.$$

To get to a rate for Spontaneous Raman scattering we start with an electric field comprised of two frequencies, $\omega_p$ and $\omega_s$, who’s magnitude is given by

$$E = E_p \cos(\omega_p t) + E_s \cos(\omega_s t),$$

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Appendix C (Continued)

where the subscript $p$ stands for pump laser and the subscript $s$ stands for Stokes. Using (A.38) we can express the electric field components in terms of the photon creation ($a^+$) and annihilation ($a$) operators as

$$E \propto \sqrt{\omega_p}(a_p^+ - a_p) + \sqrt{\omega_s}(a_s^+ - a_s).$$

(C.5)

Similarly we can expand $X$ with the harmonic oscillator creation ($a^+_\nu$) and ($a_{\nu}$) operators as

$$X \propto (a^+_\nu + a_{\nu}).$$

(C.6)

The rate of emission of a Stokes photon into a single mode is proportional to the non-zero matrix element for that process

$$W_{\text{emission}} \propto |\langle n_p - 1, n_s + 1, 1 | a_p a_s^+ a_{\nu} | n_p, n_s, 0 \rangle|^2 = n_p(n_s + 1),$$

(C.7)

where the ket is the initial state of the molecule in the ro-vibrational ground level with $n_p$ pump laser photons and $n_s$ Stokes photons and the bra is the final state of the molecule in the upper level with one less laser photon and one more Stokes photon. The rate of the inverse process, absorption of a Stokes photon, is proportional to

$$W_{\text{absorption}} \propto |\langle n_p + 1, n_s - 1, 0 | a_p^+ a_s a_{\nu} | n_p, n_s, 1 \rangle|^2 = (n_p + 1)n_s,$$

(C.8)

which results in the deexcitation of the system back into the ro-vibrational ground level and an emission of pump laser photon. From (C.7) and (C.8) we can get the rate of scattering of Stokes photons into a single mode as

$$\frac{dn_s}{dt} = DP_a n_p(n_s + 1) - DP_s n_s(n_p + 1),$$

(C.9)
Appendix C (Continued)

where \( D \) is a constant and \( P_a \) and \( P_b \) are the probabilities that the molecule is in the ground state \( \nu = 0 \) and the excited state \( \nu = 1 \). Since at room temperature \( P_a \approx 1 \) and \( P_b \approx 0 \) and for spontaneous Raman scattering \( \langle n_s \rangle \ll 1 \) (i.e. no stimulated emission), we can simplify (C.9) and get the rate of emission of Stokes photons as

\[
\frac{dn_s}{dt} = D n_p. \tag{C.10}
\]

We obtain the free space value of \( D \) from experimentally measurable values with [58]

\[
D = \frac{\nu_l N c^4}{3V \Delta \nu \nu_s^3} \frac{d\sigma}{d\Omega}, \tag{C.11}
\]

where for simplicity we set the index of refraction to 1 for all frequencies and \( \nu_p \) is the pump laser frequency, \( \nu_s \) is the Stokes frequency, \( c \) is the speed of light in a vacuum, \( V \) is the mode volume, \( \Delta \nu \) is the natural linewidth of the transition, \( N \) is the density of molecules, and \( d\sigma/d\Omega \) is the differential scattering cross section.
Appendix D Free Space CARS Rate

To get a better understanding of the CARS four wave mixing process we can develop a CARS free space scattering intensity equation by using [55] and [20] and starting with the wave equation, for the Stokes (s), pump (p) and anti-Stokes (as) waves, in an isotopic, dispersionless material and, for simplicity, set the index of refraction equal to 1 to get the relation

\[-\nabla^2 E_{as}e^{i(k_{as}z-\omega_{as}t)} + \frac{1}{c^2} \frac{\partial^2}{\partial t^2} E_{as}e^{i(k_{as}z-\omega_{as}t)} = \frac{-1}{\varepsilon_0 c^2} \frac{\partial^2}{\partial t^2} P_C^{(3)} \]

where \(P_C^{(3)} = \varepsilon_0^3 (\chi^{(3)}_{CARS} E_p^2 E_s^* e^{i(2k_p - k_s)z - \omega_{as}t})\) is the CARS third order polarization, \(k_i\) is the momentum vector equal to \(\omega_i/c\), \(E_i\) is the electric field amplitude, \(z\) is the distance of propagation with \(i\) an index for \(s, p, as\) and the complex conjugate was omitted for simplicity. Now we can assume that all electric fields involved point in the same direction and treat each as a scalar quantity. Next we take all the derivatives, along with some algebra, and make use of the slowly varying wave approximation (\(|\frac{d^2 E_{as}}{dz^2}| \ll |k_{sd} E_{as}|\)) to get to the gain equation for plane waves

\[dE_{as} = \frac{i\omega_{as}}{2\varepsilon_0 c} (\chi^{(3)}_{CARS} E_p^2 E_s^* e^{i\Delta k z} dz)\]

where \(\Delta k = 2k_p - k_s - k_{as}\) is the momentum matching condition. Now we can integrate through the interaction path length, \(L\), and use the usual relationship between intensity and electric field to get

\[I_{as} = \frac{\omega_{as}^2}{8\varepsilon_0 c} |\varepsilon_2 (\chi^{(3)}_{CARS} E_p^2 E_s^*|^2 L^2 \text{sinc}^2(\Delta k L/2)\]

This shows that the intensity of scattered light not only depends on the material, interaction length and intensity of electrified, but also the momentum matching condition. CARS has become quite useful in combustion analysis and has a considerably higher conversion efficiency than regular Raman scattering [20].
Appendix E Vibrational-Rotational Spectrum

This description of the ro-vibrational spectrum is adapted from [66]. The energy of a molecule is made up of translational energy, rotational energy, vibrational energy and electronic energy. To the first approximation these energy contributions can be considered separately [66]. Translational energy gives rise to heat and other phenomena such as Doppler broadening. Electronic energy transitions are responsible for absorption and emission usually in the ultraviolet and visible regions. And infrared absorption and regular Raman scattering result from vibrational and rotational energy.

E.0.1 Vibrational Energy

A poly-atomic molecule acts as though it consist of 3N-6 (3N-5 for linear molecules) separate oscillators, where N is the number of atoms. Each oscillator vibrates in a particular mode at the frequency specific to that mode– some modes can have the same frequency and these modes are called degenerate. They are normal modes as they do not contain elements of any other mode and each is a fundamental vibration that can be combined in a superposition to make up more complex molecular vibrations. Now we can start by describing one harmonic oscillator and, since the energy levels have been shown to be discrete, the harmonic oscillator is quantized meaning the energy levels are discrete values given by

\[ E_{vib} = (\nu + \frac{1}{2})h\nu, \]  

(E.1)

where \( h \) is Planck’s constant, \( \nu \) is the vibrational frequency of the oscillator, and \( \nu \) is the quantum number which can only take non-negative integer values. This gives rise to energy transitions of

\[ \Delta E = h\nu \]  

(E.2)
Appendix E (Continued)

Eq. E.1 corresponds to a change in quantum number, $\nu$, of $\pm 1$ which is the only transition allowed by the harmonic oscillator, however transitions where the quantum number changes by more than one do occur. This leads to the anharmonic oscillator approximation, which allows for overtone and hot band transitions and has energy levels with frequencies given by

$$\frac{E_{\text{vib}}}{\hbar c} = \bar{\nu}(\nu + \frac{1}{2}) - x\bar{\nu}(\nu + \frac{1}{2})^2 + \ldots, \tag{E.3}$$

where the bar denotes units of $\text{cm}^{-1}$ and $x$ can be determined experimentally. This gives transitions of

$$\Delta E_{\text{vib}}/\hbar c = \bar{\nu}_0, \tag{E.4}$$

where

$$\bar{\nu}_0 = \bar{\nu} - x\bar{\nu}(\nu + \nu^2) \quad \nu = 1, 2, 3, \ldots \tag{E.5}$$

The distribution of populations of energy levels for a group of molecules in thermal equilibrium can be calculated using the Boltzmann distribution and the ratio of the number in a state $i$, $n_i$, to the number in the ground state, $n_0$, is given by

$$\frac{n_i}{n_0} = e^{-\frac{(E_i - E_0)}{kT}}, \tag{E.6}$$

where $E_i$ and $E_0$ are the energy levels of the $i^{th}$ and ground state, $k$ is the Boltzmann constant and $T$ is the temperature. At room temperature, 300 K, and with $\bar{\nu} \gg 200\text{cm}^{-1}$ for most molecules, it can be safely assumed that all molecules are in the ground state.
Appendix E (Continued)

E.0.2 Fermi Resonance

In the case where an overtone or combination band has a frequency near another fundamental transition and both have the same symmetry, they can interact in a way that shifts their energy levels and changes their relative spectral intensities [66]. This is known as a Fermi resonance. The energy levels are given by

\[ E'_1 = E_1 + E_{interaction} \]  
\[ E'_2 = E_2 - E_{interaction} \]

Where \( E_1 \) and \( E_2 \) are the unperturbed energy levels. A classic example is of CO\(_2\) where one strong band is expected at the stretching overtone at 1334 cm\(^{-1}\), but instead two strong bands are seen at 1388 cm\(^{-1}\) and 1285 cm\(^{-1}\). An energy diagram representing this is given below.

![Energy levels for the Fermi resonance for the fundamental symmetric stretching mode and overtone of the bending mode for CO\(_2\) [2].](image)

Figure E.1. Energy levels for the Fermi resonance for the fundamental symmetric stretching mode and overtone of the bending mode for CO\(_2\) [2].
Appendix E (Continued)

In this text this is referred to as the $2\nu_2/\nu_1$ Fermi dyad. The lower component, in energy, is given the notation $\nu_-$ and the upper component is $\nu_+$.

### E.0.3 Rotational Energy

Each molecule contains rotational energy. In the case of a linear molecule, like CO$_2$, the first approximation to this energy can be modeled as a quantum mechanical rigid rotator, which gives rotational energy levels, in frequency (cm$^{-1}$), as

$$
\frac{E_{\text{rot}}}{\hbar c} = BJ(J + 1),
$$

(E.9)

where $J$ is the rotational quantum number, which can only assume non-negative integer values and $B$, the rotational constant, is defined by

$$
B = \frac{\hbar}{8\pi^2I_b c},
$$

(E.10)

where $I_b$ is the moment of inertia, $\hbar$ is Planck’s constant and $c$ is the speed of light. To more accurately model the energy levels, a correction term, $D[J(j + 1)]^2$, is subtracted. This term takes into account centrifugal distortion and the second approximation becomes

$$
\frac{E_{\text{rot}}}{\hbar c} = BJ(J + 1) - D[J(j + 1)]^2,
$$

(E.11)

where $D$ is the centrifugal distortion constant. Like the vibrational states, the rotational states’ populations are governed according to the Boltzmann distribution with their relative intensities given by

$$
I_J = (\hbar cB'' \nu/kT)(2J + 1)e^{-B'' \nu J(J+1)\hbar c/kT},
$$

(E.12)

where the $(2J + 1)$ term accounts for degeneracy in each state.
Appendix E (Continued)

E.0.4 Combined Rovibrational Spectrum

To get a full representation of the rotational-vibrational band, the energies of both the vibration and rotational levels described above can be added together. The sum of Eq. E.3 and Eq. E.11 gives the frequencies for each energy level as

\[ \frac{E_{\text{ro-vib}}}{\hbar c} = \tilde{\nu}(\nu + \frac{1}{2}) - x\tilde{\nu}(\nu + \frac{1}{2})^2 + BJ(J + 1) - D(J(j + 1))^2. \] (E.13)

There exist two types of rotational-vibrational bands for polyatomic linear molecules (eg. CO\(_2\)): parallel, when the change in the dipole moment is parallel to the molecular axis, and perpendicular, when the change in dipole moment is perpendicular to the molecular axis. The selection rule for the perpendicular band is \( \Delta J = 0, \pm 1 \). In the case of the so-called Q branch of the perpendicular band, the selection rule is \( \Delta J = 0 \). An equation for the spectra of the Q branch can be obtained by subtracting Eq. E.13 with \( \nu = 0 \ B = B'' \) and \( D = D'' \) from the same equation with \( \nu = 1 \ B = B' \) and \( D = D' \) where the double prime represents the values in the ground state and single prime is the values in the first excited state. This gives the spectra for the transition from the first excited state to the ground state as

\[ \tilde{\nu}_J = \tilde{\nu}_0 + J(J + 1)(B'_\nu - B''_\nu) + J^2(J + 1)^2(D''_\nu - D'_\nu), \] (E.14)

where \( \nu_0 = \tilde{\nu} - 2x\tilde{\nu} \) is the vibrational frequency in the form of Eq. E.5. Since the energy of the vibrational transitions are large, it can be safely assumed that all molecules are in the vibration ground state, so there is no vibrational distribution. However, the transition energies are smaller for the rotational levels, which means there will be a distribution of rotational states with intensities given by Eq. E.12. Therefore Eq. E.14 and Eq. E.12 can be used along with experimentally obtained values for \( B \) and \( D \) to produce a simulated spectra for Raman scattering of the Q branch \([67]\).
Appendix F Cavity Stabilization and Thermal Bistability

F.1 Cavity Stabilization

The need to maintain the cavity at an exact resonance length is crucial for cavity quantum electrodynamics experiments. Furthermore, in our experiments there is a need for a large, several microns, range in tuning of the length. To satisfy both of these needs, we employ one of two active stabilization techniques, where we lock the cavity’s length to the pump laser’s frequency.

F.1.1 Side of Fringe Locking

In this technique the cavity is locked to the side fringe of the transmission signal. If, as shown in Fig. F.1 (a), the laser’s frequency is set to the side of the cavity resonance, then a small change in cavity length produces a proportional change in transmission intensity. This can be used as a feedback signal that is sent to the piezo electric actuator to compensate for fluctuations in the cavity length and hold the cavity’s resonance frequency to the pump laser’s frequency.

![Diagram](image)

Figure F.1. (a) Transmission through the cavity with the position of the side of fringe lock labeled. (b) The basic setup for the side of fringe locking scheme.

Of course, as shown in Fig. F.1 (a), the laser’s frequency is not at the center of the cavity resonance, hence the name side of fringe. This means the main draw back of this
Appendix F (Continued)

method is that only a fraction of the light is at the cavity resonance. Furthermore, since
the lock point is dependent on the magnitude of the signal, fluctuations in the output
intensity of the laser will cause unwanted fluctuations in cavity length. See Fig. F.1 (b)
for a diagram of the setup.

F.1.2 Pound-Drever-Hall Locking Scheme

The Pound Drever Hall locking technique [68, 69] is a relatively new method for the
stabilization of laser frequency or, in our case, locking a cavity’s resonance length to the
frequency of a laser. It has the advantages over fringe locking in that it locks directly to
the frequency of the laser and it also decouples the lock point from intensity fluctuations in
the laser’s output. It works by dithering the phase, or frequency, of the laser sinusoidally
over a small range. In this way the reflection from the cavity has information both about
how far from the resonance the center, or carrier, frequency is and on which side. If we use
an optical isolator to pick off the reflection and send it into a photo detector, the signal can
be mixed with the sinusoidal oscillation modulating the laser beam’s frequency (or phase)
and an error signal will be produced that can stabilize the laser’s frequency or, again in
our case, the cavity’s length. The setup is depicted in Fig. F.2 (a).

![Diagram of Pound-Drever-Hall locking scheme](image)

Figure F.2. (a) Error signal for the Pound-Drever-Hall locking scheme with the lock point
labeled. (b) Basic setup for the Pound-Drever-Hall locking scheme.
To get a better idea of what is going on, I will provide a brief mathematical description of a phase modulated error signal. We start with the incoming electric field that has its phase modulated

$$E_{\text{inc}} = E_0 e^{i(\omega t + \beta \sin(\Omega t))}, \quad (F.1)$$

where the power is given by $P_0 = |E_0|^2$, the carrier frequency is $\omega$, the phase modulation frequency is $\Omega$ and $\beta$ is the modulation depth. Eq. (F.1) can be expanded using Bessel functions as

$$E_{\text{inc}} \approx E_0 [J_0(\beta) + 2iJ_1(\beta) \sin(\Omega t)] e^{i\omega t}$$

$$= E_0 [J_0(\beta)e^{i\omega t} + J_1(\beta)e^{i\omega t} - J_1(\beta)e^{i\omega t}]. \quad (F.2)$$

To get the reflected beam we can multiply each term by the reflection coefficient

$$F(\omega) = E_{\text{ref}} / E_{\text{inc}} = \frac{r(e^{i\omega/\Delta \nu_{\text{fsr}}}) - 1}{1 - r^2 e^{i\omega/\Delta \nu_{\text{fsr}}}} \quad (F.3)$$

where $r$ is the amplitude reflection coefficient of the mirrors and $\Delta \nu_{\text{fsr}}$ is the free spectral range of the cavity. Then we use the relation $P_{\text{ref}} = |E_{\text{ref}}|^2$ to get the power reflected as

$$P_{\text{ref}} = P_c |F(\omega)|^2 + P_s \{ |F(\omega + \Omega)|^2 + |F(\omega - \Omega)|^2 \} +$$

$$2\sqrt{P_c P_s} \{ \text{Re} [F(\omega)F^*(\omega + \Omega) - F^*(\omega)F(\omega - \Omega)] \cos(\Omega t) +$$

$$\text{Im} [F(\omega)F^*(\omega + \Omega) - F^*(\omega)F(\omega - \Omega)] \sin(\Omega t) \} + (2\Omega \text{ terms}), \quad (F.4)$$
Appendix F (Continued)

where \( P_c = J_0^2(\beta)P_0 \) is the power of the carrier beam at frequency \( \omega \) and \( P_s = J_1^2(\beta)P_0 \) is the power of both sidebands at frequency \( \omega \pm \Omega \). When this is mixed with the signal from the local oscillator, the \( \sin(\Omega t) \) term gets pulled out and the error signal is

\[
\epsilon = -2\sqrt{P_c P_s} \text{Im}[F(\omega)F^*(\omega + \Omega) - F^*(\omega)F(\omega - \Omega)] \tag{F.5}
\]

The error signal, displayed in Fig. F.2 (a), is what gets sent to the proportional integral controller. A diagram of the setup is displayed in Fig. F.2 (b).

F.2 Microcavity Thermal Behavior

Due to the high the concentration of laser power inside high finesse microcavities on resonance, they are susceptible to thermal induced nonlinearities [70]. These thermal effects have been extensively studied in solid resonators [71, 72]. They have been shown to exhibit thermal line broadening, a wavelength hysteric response and have both stable and unusable equilibriums [61]. Furthermore, there has even been several studies showing how to compensate for these thermal effects [73, 74].

For completeness we documented these effects in our microcavities. Since our microcavities have an open center, we attribute the effects to thermally induced changes in the index of refraction in the mirror and substrate [31] material (note: thermal expansion also occurs, but this effect is much smaller in magnitude than the change in index of refraction). This changes the optical path length and, hence, the resonance frequency of the cavity. The broadening depends on the the mismatch between the rate of heat build up to the rate of dissipation. At higher powers, the buildup of heat exceeds the rate at which it can be dissipated. The relationship of input power to broadened linewidth has been shown to be linear [31]. In Fig. F.3 the relative linewidth, in reflection, for several scans of the cavity’s length around the resonance length of a fixed frequency input laser is shown. The
family of curves, at four different input powers, show an exponential relationship between broadened linewidth and scanning speed at all input powers. In this case the broadening depends on the rate of build up compared to the rate of scanning. At high speed there is less time on resonance and less heat build up, which results in a narrower linewidth. The lower speeds allow the build up of heat and therefore are more thermally broadened.

The thermal induced broadening shows a hysteric response. Fig. F.4 shows the down and up voltage scans, which correspond to a shortening and lengthening of the PZT (and cavity length in this setup 3.4 (b)) respectively. On the down scan there is a narrowing. The change in index of refraction causes the optical path length to decrease and, since this is in the same direction of the PZT length scan, the linewidth is narrowed as they work together. On the up scan, the optical path length and the PZT scan are opposite to each other, which causes linewidth broadening as the index change compensates for the change in PZT length. The up scan was used in Fig. F.3.

Figure F.3. (a) The broadening for four input powers 8.7 mW, 5.2mW, 2.3 mW and 1.0 mW, at several different cavity length scanning speeds. (b) Close up comparing the most broadened lineshape to the least broadened lineshape— a difference of more than a factor of 10.
Figure F.4. Top: the reflection dip during a cavity length scan over the resonance with an input power of 13.8 mW and scanning rate of 1115 Hz. Bottom: PZT voltage.

Due to this response there is also an equilibrium point on the broadened side where the thermally induced change in index of refraction compensates for small drifts in the resonance length [75]. We took advantage of this by using the side of fringe locking technique in our experiments, which simplified the locking implementation over the previously used Pound-Drever-Hall method.
Appendix G List of Publications

G.1 Journal Articles


Appendix G (Continued)

G.2 Conferences


• B. Petrak, N. Djeu, and A. Muller, “Purcell Enhanced Raman Scattering from Atmospheric Gases in a High-Finesse Microcavity” Paper presented at: The Conference on Lasers and Electro Optics (CLEO: 2013); 2013 June 8-13; San Jose, CA

• B. Petrak, K. Konthasinghe, S. Perez, and A. Muller, “Feedback-Controlled Laser Fabrication of Micromirrors”, Poster presented at: The Conference on Lasers and Electro Optics (CLEO: 2012); 2012 May 6-11; San Jose, CA

• B. Petrak, K. Konthasinghe, S. Perez, and A. Muller, “Purcell Enhancement of Raman Scattering in a High-Finesse Microcavity for Gas Sensing”, Paper presented at: APS March meeting; 2012 Feb. 27 - Mar. 2; Boston, MA
ABOUT THE AUTHOR

Benjamin Petrak was born on September 26, 1981 in Ashtabula, Oh and graduated from Mt. Vernon Senior High School in 2000. He earned his B.S. in physics from The Ohio State University in 2006 and subsequently his M.S. in financial mathematics from The Florida State University in 2008. He became a pricing actuary at Bankers Insurance Group in 2008 and quit to enter the applied physics program at The University of South Florida in 2010. He was awarded a M.S. in applied physics in 2014.