

# Using FM methods with molecules in a high finesse cavity: a demonstrated path to $<10^{-12}$ absorption sensitivity

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## I. Introduction and Overview

This paper represents an effort by the authors as developers of sensitive absorption techniques to make these ideas and strategies available to the wider community, especially to those colleagues in whatever field who have real scientific problems which could be advanced if only they had available a higher level of absorption sensitivity. We have a few such scientific and/or applications areas in mind ourselves and, indeed, most of this work has been motivated by one of them: the dream of having a general method to produce a high performance frequency reference basically anywhere in the visible/near ir domain. For this, molecular overtones recommend themselves because of their generous spectral coverage, but it is only with the development of these ultrasensitive absorption measurement techniques that this application has been heading for fruition.

### High sensitivity is interesting for ...

There are many, many interesting applications for spectroscopic techniques, and there tends to be a general explosion of applicability when the sensitivity gets into today's ppT ( $10^{-12}$ ) domain. We can note just a few to give a flavor.

**Atmospheric detection of trace materials:** An "easy" application of laser spectroscopy is to explosion-hazard assessment. Spectroscopically at least, it is easy since the ir fundamental bands of ubiquitous gases such as  $\text{CH}_4$  are very strong. Of course, making reliable and appropriate laser equipment can be a serious challenge here, since the natural laser of choice, the tunable semiconductor laser has not yet been well-perfected in the 3.0-3.2  $\mu\text{m}$  range. Some systems have been built using the 3.39  $\mu\text{m}$  HeNe laser, but we suppose that future systems will in fact use the well-developed diode lasers at 1.55  $\mu\text{m}$  as the source, even though the absorption strength on the C-H stretch overtone may be 100-fold diminished from that of the fundamental. The point is that the explosion limits are in the percent range, so sensitivity should not need to be a big problem for the designer.

Pollution sensing is a next opportunity, more demanding since many materials are hazardous in concentrations at even the ppm ( $10^{-6}$ ) level. Taken with the complexity of molecular spectra and strong broadening by atmospheric pressure, these applications begin to be more "interesting" for the instrument designer.

A new spectroscopic industry is health-testing via identifying specific metabolism-related gas emissions in exhaled human breath. For example, an active asthma patient exhales pentanes[1] and highly energetic molecules such as  $\text{H}_2\text{O}_2$  [2]. Ethane and pentanes[3] are widely found in human breath, appear in juvenile cases of vitamin E deficiency[4], and are believed to originate from the peroxidization of lipid cells by free-radicals within the body. Indeed some

studies consider such emissions as possible early markers for cancer[5]. Some confusion arises due to lack of chemical specificity of present tests[6].

**Molecular spectroscopy / overtones and combination bands:** Of course we collectively operate a huge industry to study the spectra of molecules. Current interests include a priori calculation of actual energies of overtone bands. Combination bands in particular are of interest, since they may give some insight into the really fundamental questions of molecular interactions and a first glimpse into a deeper understanding of chemical reaction pathways. Specific interesting spectroscopic questions here relate to large-amplitude coherent molecular vibrations, perhaps laser-induced, and the associated questions of atom exchange, symmetry effects, etc. As users of molecular overtones for frequency standards work[7], mentioned earlier, our sure destiny is to provide some precise molecular overtone parameters for the scientific community.

**Fundamental tests:** An important, albeit perhaps not urgent, fundamental application is setting better limits on the symmetrization postulate. For example some recent studies[8] showed that even levels of the O<sub>2</sub> antisymmetric ground state are not occupied, with a sensitivity  $\sim 5 \times 10^{-7}$ . The sensitivity limit was associated with the relatively low absorption strength of the “forbidden” 760 nm band, and the simple direct absorption methods utilized for these first studies. With a high finesse cavity to enhance the absorption, probably 3 or more orders of magnitude will be added to the evidence that molecules are not to be found in the symmetry-forbidden states.

An even more speculative concern is for possible discrepancies between different quantum clocks, based on potentially different response of their internal “clock mechanism” to changes in: a) gravitational potential; b) epoch after the Big Bang; c) putative difference in interactions based on Baryon/Lepton ratio, “new physics” etc. This is the quantum clock-builder’s playground!

## II. Optical Heterodyne Detection

### What is optical heterodyne detection ?

In the photo-detection process, we know that photons absorbed give rise to electron-hole pairs in the semiconductor. Ideally a very high fraction,  $\eta$ , of these are separated before recombination, and are separately routed to the device terminals by internally-generated or externally-imposed bias fields. So the expected signal current from this process is easily written as  $i = \eta e P / h\nu$ , where  $i$  is the external current,  $P$  the detected light power,  $e$  the electron charge and  $h\nu$  is the photon energy. Silicon and InGaAs detectors with a value of quantum efficiency  $\eta > 0.9$  are available at reasonable cost commercially. Before considering the noise of the process, we note that the optical power will generally have a time-dependent term if the applied laser field is the sum from two sources, ie  $P(t) = A I = A c/2\pi \cdot (E_1(t) + E_2(t))^2$ . Here  $A$  is the effective area of the laser intensity  $I$ , and we will neglect important interference details by assuming the two contributing fields to be mutually mode-matched. With  $E_1(t) = E_1 \cos(\omega_1 t)$  and similarly for  $E_2$  and  $\omega_2$ , when the difference of the two applied frequencies is within the detector’s response bandwidth, we expect a detected photocurrent of the form  $i(t) = (i_1 + 2 \sqrt{i_1 i_2} \sin(\omega_1 - \omega_2) t + i_2)$ . We refer to this cross term at the difference frequency as the heterodyne response. If we had chosen to think of the field  $E_2$  as somehow different, for example it was a weak field being produced by a molecular sample, one can see one of the advantages of the heterodyne approach: the scale of the beat current can be increased as we like by increasing the size of  $E_1$ , which is referred to as the “Local Oscillator” field, following the practice in radio-frequency engineering. It is fundamental that the S/N is not degraded by use of a larger LO power. Some technical remarks below return to this subject.

### How does heterodyne detection reach the limits of fundamental noise ?

Any real physical photodetector will offer some output noise even in total darkness. If we attempt direct detection of a weak signal, the incident POWER will need to be sufficient to give a photodetected current which can mask the detector's noise. Consider the heterodyne case: now the signal-bearing light power is represented by the cross-term between the Local Oscillator field and the weak signal field. It is only this PRODUCT which needs to be adequately large to mask the detector noise. So by merely using a stronger Local Oscillator (LO) field, we can overcome some appreciable noise, typically produced by the amplifier circuit which converts the photocurrent into an output voltage.

Of course, this Local Oscillator power can carry laser intensity noise to the detector as well. Any non-fundamental noise imposed on this intensity will be directly converted into an unwelcome output noise. But typically this noise, which we may call "technical noise" to identify its origin, is concentrated at lower frequencies. Everyone has heard some discussion about "1/f" noise sources. Even though technical noise seldom has such a pure spectrum, it does carry a spectral density which is concentrated mainly at power-line harmonics and other low frequencies associated with laboratory vibrations. Various noise processes in semiconductor devices are also restricted to low audio frequencies and below. So an important idea in achieving low noise performance is to place the information-carrying heterodyne signal at a frequency sufficiently high that a negligible level of technical noise is carried by the LO field. Before illustrating noise levels of actual lasers, it is useful to be quantitative about this heterodyne idea.

### **What are the physics limits ?**

Even in the absence of noise of technical origin, one can observe a fluctuating component of photocurrent when the input light level appears to be ideally steady. Some years ago a radio-engineering explanation of this residual noise would note that the current in the photodiode is actually carried by discrete charged particles, mainly the electrons in view of their higher mobility, and one would associate an irreducible SHOT-NOISE with their fluctuation. A standard formulation would provide the result

$$i_n^2 = 2ei_{dc}B \quad (1)$$

where B is the bandwidth within which the fluctuating current  $i_n$  is observed, and  $i_{dc}$  is the average photocurrent. While this is indeed the correct answer, there are two important remarks. Firstly, we do not expect to see shot-noise fluctuation currents in some current carried in a simple wire or resistor: this current is carried by a swarm of coordinated charges, something like a slowly-moving "Jello" cloud of electrons. The effective number is huge, while the effective velocity is very small. So the number fluctuations are negligible. Secondly, an entire industry has grown up recently in physics in which the radiation field is "squeezed" to provide sub-shot-noise levels of fluctuation. Surely this would have been a frustrating business if the electron graininess were the real source of the current fluctuation: one simply could not have seen a sub-shot-noise current fluctuation below the limit of Eq. 1. In fact, the "real" source of the fluctuation is that the quantized radiation field interacts with matter in a discrete way. The field can be carrying Poissonian statistics, such as light from a thermal source or a laser far above threshold, or it may have sub-Poissonian levels of fluctuation, providing a more regular rate of photo-electron generation and so an anomalously low fluctuation level for the photocurrent. One should think of the electron as "jumping" when the field commands it: this means that "squeezing"-like processes can only be observed when the photodetection quantum efficiency is high. But here our task is just to be able to approach the standard shot-noise level in our spectroscopy. Of course, if the quantum efficiency of the detector we choose is seriously low, we will be measuring a lower current, and it will therefore have a higher relative fluctuation than was demanded by any fundamental limit. Next year: squeezing!

### Shotnoise limit: the highest possible sensitivity in direct absorption

The fluctuating current noise, shot-noise calculated above, will set the fundamental sensitivity limit for straight absorption spectroscopy. Taking the S/N as 1, the molecular absorption needs to be equivalent to the shot-noise in the measurement bandwidth. This gives

$$i_{dc} \cdot \alpha L = \sqrt{i_n^2} = \sqrt{(2 e i_{dc} B)}, \text{ so we obtain the minimum detectable absorption as}$$

$$(\alpha L)_{\min} = \sqrt{\frac{2eB}{i_{dc}}} \quad (2)$$

To make this concrete, according to Eq. 2 we should be able to detect an integrated absorption of  $1.8 \times 10^{-8}$  with a shot-noise-limited photo current of 1 mA, using a 1 Hz measurement bandwidth. Needless to say, this feels optimistic compared with experience.

### What are the real (technical) limits ?

Of course, it is easy to observe that actual lasers display vastly more noise than any fundamental shot-noise limit. We dismiss immediately the silly causes such as inadequate smoothing of power-supply potentials, even though these are basically always an issue in an actual lab experiment. Laboratory vibrations modify the laser's alignment and so record their presence on the output power. High voltage discharge lasers often have a few deciBels increased noise due to fluctuation of the resistance of the high-voltage ballast resistor (which should be wirewound, not carbon composition, to avoid this degradation.)

A modern trend is the use of a pump laser, such as a diode laser, to provide laser pumping for some more stable, but tunable, laser for our spectroscopy. A typical example is pumping a Ti:Sapphire laser with an Ar<sup>+</sup> ion laser. A new possibility is to pump the Ti:Sapph with a diode-pumped solid state laser, for example laser-diode-pumped Nd:YVO<sub>4</sub> which is frequency-doubled into the green[9]. Such lasers - at the 5 W level ! - are available from two US firms at present. We show data measured with our JILA-designed ring Ti:Sapphire laser pumped by the "Millennium" laser.[10] The photodetected current was amplified by a transimpedance amplifier of 85 kohms with an ac-coupled 43 ohms series resistor in the rf output. Thus the 3.47 V dc level corresponds to a 40.8 μA dc photocurrent. (All three traces were taken at the same DC level.) The calculated rms shot-noise voltage level produced by the amplifier is 0.307 μV, yielding across the 50 ohm input of the spectrum analyzer some 50/(50+43) of this, or 0.165 μV. This represents -122 dBm noise power in a 1 Hz bandwidth. Since the measurement bandwidth was actually 1 kHz, our calculated shot-noise output should be 30 dB higher, viz -92 dBm. In fact, this is the observed value at high frequencies: see Fig. 1. The trace labeled "shot-noise" was taken with illumination by a flashlight, so the noise increase at lower frequencies (<20 kHz) shows some deficiencies of our detector/amplifier system. The trace labeled "Millennia" shows that the diode-pumped solid state laser approach[10] can produce a low level of light noise, only a little above the shot-noise level of our measured ~100 μW of light. However, since the laser output is actually 5 W, some 50,000-fold (+47 dB) larger, this laser's output is in fact far from being "shot-noise-limited." Still, it is one of the quietest pump lasers we have measured so far. The 5 W pump light brought our Ti:Sapph laser to 200 mW output at 780 nm, and the noise of a 100 μW sample of this light is also displayed. The broad bump around 200 kHz is the "relaxation oscillation" associated with energy exchange between excited Cr<sup>3+</sup> ions and photons in the laser cavity. The narrower features are due to several modulations and their widths, and that of the zero-frequency feature, are associated with the 1 kHz resolution level utilized for the spectral analysis. **So the message is: do the detection at high frequencies where the excess noise has basically disappeared.**

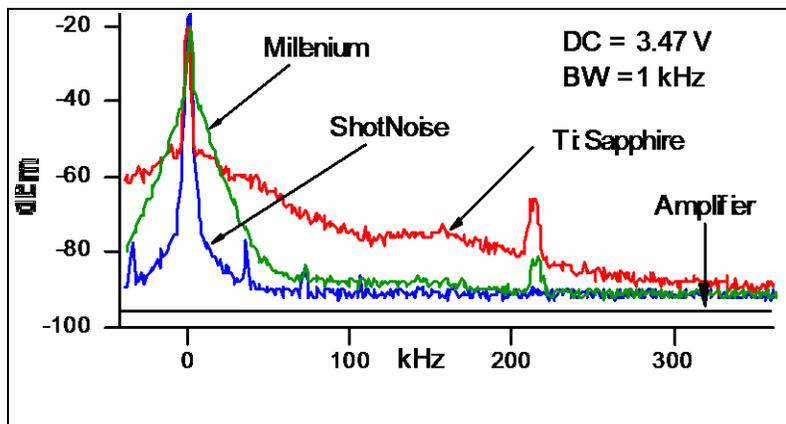


Fig. 1. Intensity noise of JILA-designed Ti:Sapphire ring laser pumped by a commercial diode-pumped Nd:YLF solid-state laser (Spectra-Physics “Millenium” [10]) system. Comparison curves are shot-noise from the same light level provided by flashlight, and actual intensity noise of green output of the DPSS Millenium system. Detected light power approximately 100  $\mu$ W.

### III. Sensitivity Enhancement by an Optical cavity

With the aim on further enhancing the detection sensitivity of the optical heterodyne spectroscopy discussed in section II, here we present another sensitivity-boosting technique, namely cavity absorption-enhancement spectroscopy where an external resonator is used to contain both the sample gas and the light field to enhance the light-matter interaction.

It was realized in the early days of laser development that a laser cavity can be used to greatly enhance the absorption detection sensitivity.[11] Basically the advantage comes from the multipass effect and the delicate balance between the laser gain and intracavity absorption.[12,13] However, it is now often preferred to separate the absorber from the laser in order to extend the experimental flexibility and to have better controlled working parameters. Enhancement of absorption sensitivity has been accomplished by using long multipass absorption cells.[14] Kastler suggested a Fabry-Perot cavity could be used because its transmission is sensitive to small variations of its inside absorption.[15] For high-resolution, Cerez *et al*[16] first applied this external cavity technique to saturated absorption spectroscopy. Ma and Hall[17] were able to use an external resonator combined with the optical heterodyne spectroscopy to achieve excellent signal-to-noise ratios. The use of an external cavity for the detection of molecular overtone transitions was also demonstrated later.[18] In linear-absorption experiments, an enhancement cavity has been used most extensively in the context of ring-down spectroscopy.[19] (See section IV for further discussions)

The advantages of using an external optical resonator are manifold. First of all, the light travels many times through the intracavity absorber so that the effective absorption length is increased by the factor of  $(2 \cdot \text{Finesse}/\pi)$ . This directly increases the detection sensitivity. Secondly, the cavity builds up its intracavity power. This allows the use of low-power lasers for the input, even for the weak transitions which require large intensities to saturate. It also reduces the output power level that needs to be handled by a photodetector. In addition, the geometrical self-cleaning and matching of the two counter-propagating waves inside the cavity are important both for eliminating pointing-direction-related noises and for obtaining narrow and unshifted resonance lines, as explained by Hall and Bordé.[20] Furthermore, a stable cavity can be used to pre-stabilize the laser frequency when it is locked on a cavity resonance, thereby reducing the detection noise.

Figure 2 shows a standing wave optical resonator. The input coupling mirror has a power transmission coefficient of  $T_{in}$  and loss of  $L_{in}$ , while for the output coupler they are  $T_{out}$  and  $L_{out}$ , respectively. The total empty cavity loss is  $L_{cav} = T_{in} + T_{out} + L_{in} + L_{out}$ . We denote the optical

input power as  $P_{in}$ , the cavity-reflected power as  $P_r$ , and the cavity-transmitted power as  $P_t$ . The cavity finesse ( $F$ ) is simply

$$F = \frac{2\pi}{L_{cav}} . \quad (3)$$

The (resonant-) cavity reflection efficiency ( $R_{cav}$ ), transmission efficiency ( $T_{cav}$ ), and intracavity build-up power can be expressed as

$$\begin{aligned} \frac{P_r}{P_{in}} = R_{cav} &= (L_{in} + L_{out} + T_{out} - T_{in})^2 \left( \frac{1}{L_{cav}} \right)^2 , \\ \frac{P_t}{P_{in}} = T_{cav} &= 4T_{in}T_{out} \left( \frac{1}{L_{cav}} \right)^2 , \\ \frac{P_c}{P_{in}} &= 4T_{in} \left( \frac{1}{L_{cav}} \right)^2 . \end{aligned} \quad (4)$$

Figure 2 also shows the enhancement of absorption contrast by the cavity. The cavity length is  $L$  and it is filled with a weakly-absorbing gas sample with an absorption coefficient of  $\alpha$  per unit length. By weakly-absorbing we mean the cavity round trip loss due to the sample is:  $1 - \exp(-2\alpha L) \approx 2\alpha L$ . In a direct absorption measurement with a plain gas cell of length  $L$ , the output power is:  $P_{out} = P_{in} \cdot e^{-\alpha L} \approx P_{in} (1 - \alpha L)$ . Therefore the absorption signal is  $P_{in} \cdot \alpha L$ , while the shot-noise is determined by the overall output power  $P_{out} \approx P_{in}$ , in the weak absorption limit. Following Eq. 2, the noise-equivalent minimum absorption sensitivity for a cell is thus:

$$(\alpha L)_{\min} \approx \sqrt{\frac{2B \cdot h\nu}{\eta P_{in}}}. \quad (5)$$

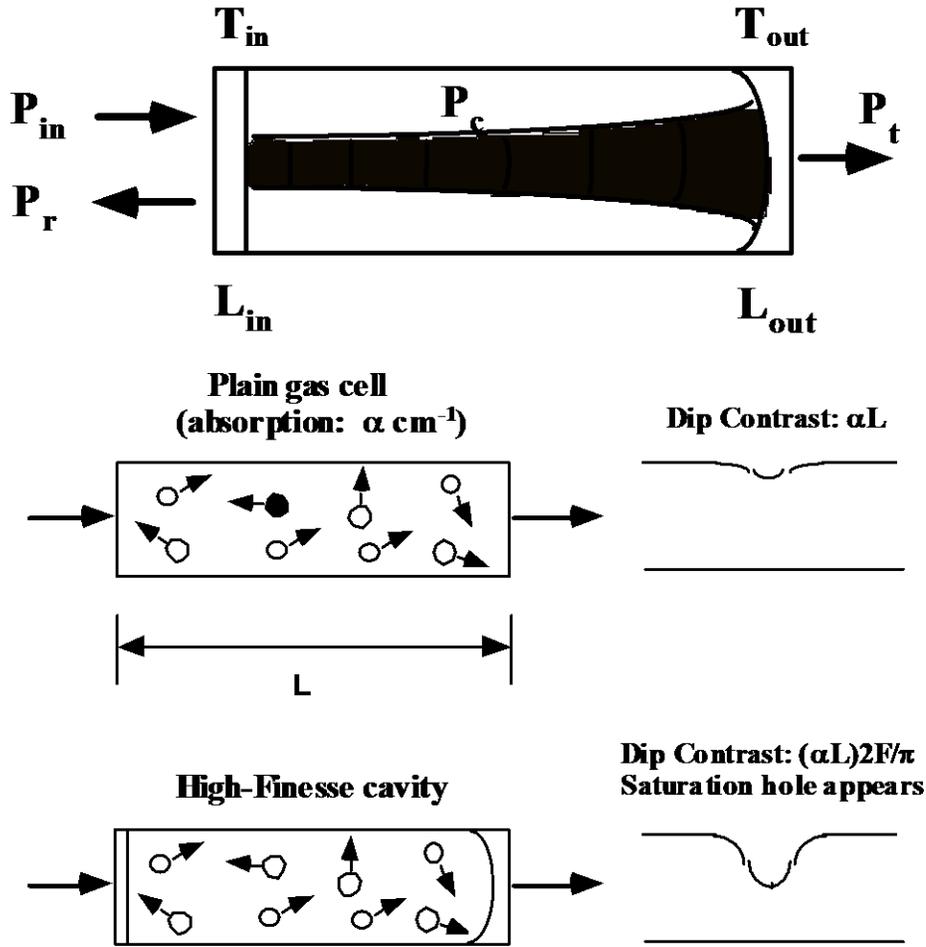


Fig. 2. Notations used for the build-up cavity. Also shown is the comparison of absorption contrast between a plain gas cell and a high-finesse cavity.

When the sample is placed inside a cavity, the transmitted power is modified from Eq. (4)

$$\frac{P_t}{P_{in}} = 4T_{in}T_{out} \left( \frac{1}{L_{cav} + 2\alpha L} \right)^2 \approx \frac{4T_{in}T_{out}}{L_{cav}^2} \left( 1 - 2\frac{2\alpha L}{L_{cav}} \right). \quad (6)$$

The detected signal contrast in the cavity transmission is therefore enhanced,

$$\frac{\delta P_t}{P_t} = 2 \frac{2\alpha L}{L_{cav}} = \frac{2F}{\pi} \cdot (\alpha L). \quad (7)$$

The associated minimum detectable absorption is hence reduced by the cavity enhancement factor of  $(2 \cdot \text{Finesse}/\pi)$ , leading to

$$(\alpha L)_{\min} = \frac{\pi}{2F} \cdot \left( \frac{2Bh\nu}{\eta P_t} \right)^{1/2} = \frac{\pi}{2F} \cdot \left( \frac{2Bh\nu}{\eta T_{cav} P_{in}} \right)^{1/2}. \quad (8)$$

The mirror parameters can be pre-designed to maximize the resonant cavity transmission  $T_{cav}$ , by taking into consideration of the intracavity gas absorption. It is clear from Eq. (4) that the in-

tracavity circulating power can be much larger than the input power. This power buildup is essential to have an appreciable level of saturation for very weak transitions to resolve sub-Doppler resonances. The strong light field drives phase-coherently the molecular dipole moments. The radiation from these prepared dipole moments is essentially the signal we want to detect. However, the strong background of the un-absorbed incoming light sets the detection shot-noise level. With the buildup cavity approach, one has a strong field for sample preparation, but it appears reduced after the sample has been prepared and the LO field is detected. When the cavity is tuned onto a molecular line, a major part (determined by the cavity efficiency) of the molecular signal will leak out of the cavity to reach a detector, while a similar (or smaller) portion of the input power will be transmitted by the cavity and reach the same detector to set the shot noise limit. The large intracavity buildup power, however, will remain trapped inside, after having prepared the phase-coherent molecular dipole moments. This result, although explained here from a different but more fundamental perspective, is intrinsically the same manifestation of the cavity enhancement effect, as discussed in the previous paragraphs.

From the technical side, the advantage of the cavity is also clear when the laser source has a relatively large amplitude noise. Then, to approach shot-noise limited detection, the optimum intensity range tends to be pushed to a lower value. Fortunately with the buildup cavity, the detector does not have to receive the large intensity. This effect is similar to the result of polarization spectroscopy<sup>21</sup> or interference filtering. Usually a reasonable power level of cavity transmission can be easily found to operate in the shot noise limited regime.

#### IV. Weak Absorption Measured By Field-Decay (Time Domain)

According to the principles of Sec. II, it is clear we should use heterodyne methods to measure an interesting optical electric field, and we should organize the measurement to produce a time-dependent signal with its principal Fourier frequencies high enough to avoid most of the laser's excess or technical noise. A natural method for doing this in a transient regime is to look at the light reflected from an optical cavity while the laser frequency is being scanned through the resonance. Such a signal is presented in Fig 3. In this case the frequency scan was basically linear so that the measured beat frequency increased with time.

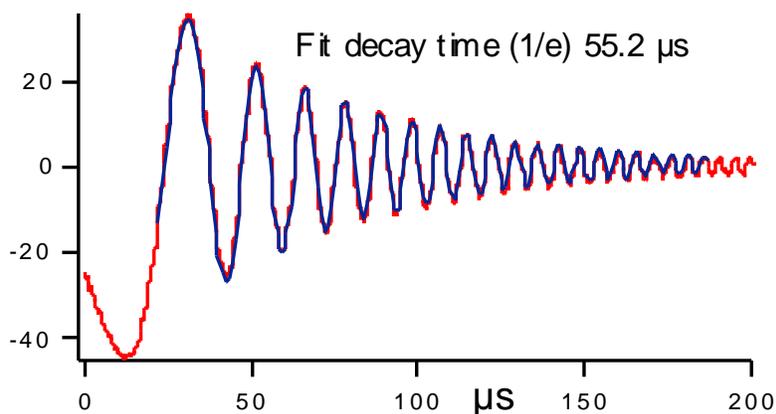


Figure 3. Cavity beating-decay, in reflection (optical heterodyne detection), with fit. We are viewing laser light reflected by a resonant cavity, after the cavity was excited when the laser frequency swept through its resonance. As the laser continued to sweep, the beat frequency between cavity-stored light and the currently-applied field continued to increase: fit improved with a small quadratic time term.

What is beating here? What optical fields are mixing in the photodetector to produce this time-dependent wave? One is the continuously-supplied exciting (and frequency-sweeping) field, serving here as our LO for the heterodyne detection. This incident field is mainly just reflected from the cavity's input mirror to reach the detector via a beam-splitter or optical circulator. It is beating with the leakage field from the cavity, which is still ringing with the energy that entered as

the laser passed through its resonance. So we are measuring the cavity's optical electric *field* decay and, of course, this field-decay transient will persist 2-fold longer than a power transient. Evidently, being able to measure the waveform longer in time can be translated into lower bandwidth, and consequently lower noise.

### **The limitations of cavity ring down spectroscopy**

We can estimate the S/N performance ideally obtained in cavity ring-down spectroscopy (CRDS) from a shot-noise limitation. From the above arguments we would like to choose a really high finesse, as then the ringing time is extended and the effective bandwidth and noise can be reduced, in a square-root fashion. There is also a linear win in the depletion of the internal cavity energy by the extra passes, but unless we can measure the cavity field and the molecule-emitted field separately there will be no particular advantage of an outrageously high finesse.

Unfortunately no research group has even approximated the associated theoretical sensitivity level using CRDS. Why? The reason is associated with the obviously-inconvenient expedient of conventional ringdown spectroscopy: the cavity+sample ringdown decay is obtained at a different time-epoch from the cavity-alone reference decay. Even if we have no non-fundamental noise in the measurement of the decays, there could easily be a serious time interval for laser re-tuning to an absorption-free wavelength. An even worse alternative would be to evacuate the sample cavity. It clearly is unreasonable to expect the cavity's losses to remain constant - at the ~ppm level characteristic of a typical shot-noise limit. The mirrors are evolving in time, and the longer the time separation of the two measurements, the more likely it is that the difference in two ringdown curves will be contaminated by systematic effects, in addition to any molecular absorption.

In fact, in our experience, even larger changes of apparent cavity finesse can easily be produced by changes in the input mode-coupling. We suppose the cavity field is then excited in a variety of its spatial eigenmodes, each of which has a slightly different round-trip phase-shift. The combined field thus can decay with spurious mode-beating phenomena, particularly if we make the recommended heterodyne measurement with the reflected excitation field. It is in principle also possible for figure defects of the cavity mirrors (and scattering) to lead to an evolving spatial distribution of the energy stored within the cavity, which would impact the heterodyne efficiency of the detection process in a time-dependent manner, thus additionally confusing the ringdown picture.

We have also observed that it is difficult to use averaging on these wiggling curves: any phase defects and one finds the decay time is artificially reduced. Even the laser phase noise would enter in this way: one needs a laser coherence time much longer than the cavity ringing time in order that successive traces can be amplitude-summed. This means that to use a simple summation, the laser linewidth would need to be considerably less than that of the cavity: If we *were* in this situation, it would be preferable to use the FM methods to be discussed momentarily.

### **Separating the cavity field from the molecular contribution**

It is provocative to think of the molecules also as sources of optical electric fields. They are immersed in a traveling field, say for example the one-direction traveling wave within the ring-down cavity. This field interacts with the molecule's electron cloud, leading to an oscillating dipole moment driven by the applied field. Of course these oscillating charges also radiate a field, each atom radiating in its preferred dipolar pattern. Summed together, there is a coherent molecular contribution only in the forward direction, and it carries the same spatial mode as the drive field. Importantly, its radiation phase is opposed to the drive field. One may usefully return to this molecular response as leading to a "darkness wave" emitted in anti-phase to the driving field. (This phase relationship ensures the attenuation of the wave as represented by the Beer's law.) So

at some distance  $L$  downstream, for small absorption we have the applied field, say normalized to unity, and the radiated field is  $-\alpha L/2$ , both oscillating with the same frequency. The downstream power will be  $(1 - \alpha L/2)^2 = 1 - \alpha L$ , as one expects. We are doing optical heterodyne detection with a zero beat frequency!

To emphasize the physical reality of this molecule-emitted darkness wave, we consider the case where there has been a step change of the frequency of the applied field. Now the dipole radiation field and the applied field will experience temporal phase reversals, since the dipole can only continue oscillating at its natural frequency, while the applied frequency is now different. One sees a Free-Induction Decay Transient, known first in NMR. Figure 4 shows data from a 1980 JILA experiment[22] exciting HF molecular dipoles with a color center laser at  $\sim 2.6 \mu\text{m}$  wavelength. As indicated, the laser contained an intra-cavity Pockels cell which allowed its frequency to be stepped to a new value in a very short time. This new field propagates through the absorption cell basically without further interaction with the originally-resonant molecules, and serves as the LO field for heterodyne detection of the HF-emitted darkness field.

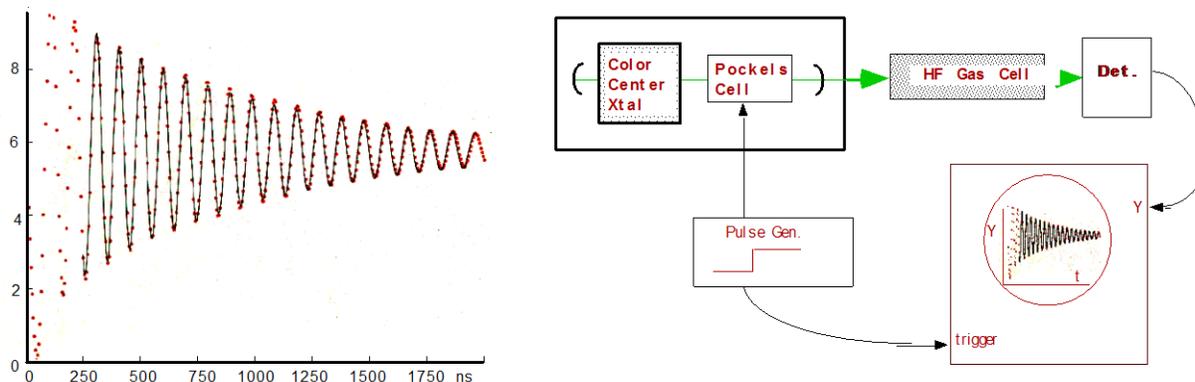


Figure 4: Free-Induction Decay of HF molecules. The laser frequency finds a particular molecular velocity which Doppler shifts the laser into resonance. These molecules become partially saturated and their dipoles continue to emit coherently even when the exciting frequency is abruptly switched away from this (velocity) group, leading to a decay beat wave at the frequency by which the laser jumped.

### Cavity-enhanced coherent transient spectroscopy

Consider the Free Induction Decay of HF molecules shown in Fig. 4. In view of the low pressure broadening ( $\sim 10$  mTorr), the laser is able to interact mainly with only a narrow velocity range of molecules. These develop a significant dipole moment, leading to radiation in the forward direction which, incidentally, accounts on a microscopic basis for the absorption indicated in Beer's law. When the laser frequency is jumped to a new value, the radiation from this coherent dipole moment overlaps in the forward direction with the exciting laser, now at a new frequency, and so we observe the beat frequency current in the photo-detected laser power. The observed decay envelope is then that of the dipoles' electric field, and contains contributions due to collisional and laser frequency broadening during preparation of the dipole moment, and damping due to transit effects and collisions during the free-precession decay. As noted earlier, if we tried to average this waveform, laser phase noise after the switching would also degrade the ringing time. Because the recorded waveform has many extrema in a decay time, we obtain many samples of the decaying amplitude, i.e. there is amplitude information, to a greater or lesser degree, in all the recorded points. When the frequency is sufficiently stable (or predictable) it seems beneficial to fit all these data. The oscillating signal makes it sure we will be aware of any residual electronic effect that makes for a baseline decay following some optical power transient reaching the photo-

detector system. Basically we have come to (Molecular) Ring-down Spectroscopy, with heterodyne detection!

### **Details of intracavity molecular spectroscopy: collision effects**

To enhance the contrast, these molecules would be contained within a low-loss buildup resonator, which also would have an exponential decay. While this seems like an extra concern, there are some interesting factors to note. First, as indicated earlier, the circulating field inside the resonator is much stronger than the input field, say 300-fold. Thus in its response, the molecule offers a 300-fold larger electric field for us to detect, for the same time-averaged power on the detector, and hence the same shot-noise level. Secondly, the observed combined decaying field is simply the sum of two fields with two decay rates and can be separated by varying the gas pressure. The clearest case comes up when the gas pressure is high enough that the molecular absorption is pressure-broadened to match the full Doppler width. This will usually occur for pressures higher than  $\sim 30$  Torr. In this domain the absorption is now homogeneously broadened, with each molecule changing its velocity often enough to participate in the absorption process. The saturation intensity has been increased by the linewidth ratio squared, so very high finesse and power buildup could be used even for strongly-interacting molecules. Now it is the molecules which have a very short dipole coherence decay time, and they may add but little ( $\sim$ few ns) to the long ringing time obtained with modern mirrors and reasonably long cell lengths. For the remainder of the cavity ring-down transient they merely serve as a nearly-equilibrated source of cavity damping: this is the usual model for CRDS. For pressures well below this range the behavior will be much more complicated for cavity ring-down spectroscopy, due to partial resolution of the Doppler profile into many velocity packets, and transition saturation effects. So quantitative absorption studies will need to take additional physics into account, and the ringing decay may reflect in part coherent storage in both the cavity field and the molecular dipoles, ie. the cavity ringdown waveform will potentially need a significant correction due to the dipole coherent contribution.

This leads us to the next discussion of a good way to coherently observe the molecular signal in the forward beam - which contains all the information - the NICE-OHMS method[23]. This acronym means Noise-Immune, Cavity-Enhanced Optical Heterodyne Molecular Spectroscopy!

## **V. Weak Absorption Measured By Field-Phase (Phase Domain)**

In the previous section the advantage of an enhancement cavity is explored in the time domain. Complementarily, the signal leaking out of the cavity can also be investigated using phase sensitive detection methods. The field phase of the light beam, associated in its form with the cavity resonant structure, is inevitably perturbed by the molecular radiation which leads to additional phase shifts. It is indeed the goal of this section to bring the phase-sensitive optical heterodyne spectroscopy into the signal recovery process using an enhancement-cavity. The fundamental advantage of this approach lies in the characteristic property of FM spectroscopy: the simultaneous observation and subtraction of the signal and background optical phases in a continuous fashion. Basically one makes temporally-local comparisons of the between on-resonance and off-resonance cases.

As one contemplates on how to probe the external cavity signal with the FM technique, the first modulation approach comes to mind is simply to lock the laser frequency tightly on the corresponding cavity resonance and then modulate the cavity mode around the desired molecular resonance while monitoring the cavity transmission. Essentially this approach is a simple lock-in derivative-lineshape recovery process. In order for this method to be successful, it is important to have a super-tight frequency lock loop between the laser and the cavity since any laser frequency

noise relative to the cavity will be converted to amplitude noise in detection. A piezo-electric transducer mounted on one of the cavity mirrors can be used to modulate the cavity length and the laser will track this modulation. The modulation frequency is usually limited to the audio range due to the mechanical resonance and roll-off of the PZT and mirror assembly. Depending upon the laser (amplitude) noise spectral distribution, the attainable modulation frequency may be too low to reach the shot-noise-limited spectral region. The intrinsic lineshape would also be modified (broadened) by this modulation process. However, attractive results have already been obtained in our experiment. Our solid-state Nd:YAG laser is locked onto our high-finesse (100,000) cavity with  $\sim 1$  milliHertz relative linewidth. A cavity-dither (at 500 Hz) and lock-in detection yields a detection sensitivity of  $3 \times 10^{-11}$  ( $6.4 \times 10^{-13}$ / cm) at 1-s averaging. This is already more than 1000 times better than typical ring-down results.

### Principle of NICE-OHMS

To be tuned more towards the true spirit of FM spectroscopy (and enjoy its noise-reduction advantages), one needs to increase the phase-modulation frequency of the probing field, usually to be much larger than the resonance linewidth under study. Besides the laser-cavity locking issue, we are then faced with another obstacle, namely the cavity bandwidth limit. What is needed is a way to have the FM sidebands at a high frequency to get low amplitude noise, while the cavity accepts the sidebands in exactly the same manner as it accepts the carrier so as to reduce the FM to AM noise conversion. This can be accomplished by frequency modulating the input laser beam at exactly the splitting frequency of the cavity free-spectral-range (FSR). We then detect and demodulate the cavity-transmitted light at the modulation frequency. The small residual frequency variations of the laser will still lead to some amplitude fluctuations and small optical phase shifts of the transmitted carrier, but they will also lead to exactly the same amplitude fluctuations and phase shifts of the sidebands which are transmitted on adjacent or nearby cavity axial orders. So the transmitted light still accurately represents an FM spectral triplet, with minimal AM conversion due to the relative laser/cavity frequency jitter. Thus the noise level can approach the intrinsic AM noise level of the laser at the FSR frequency, typically a few hundred MHz or a few GHz.

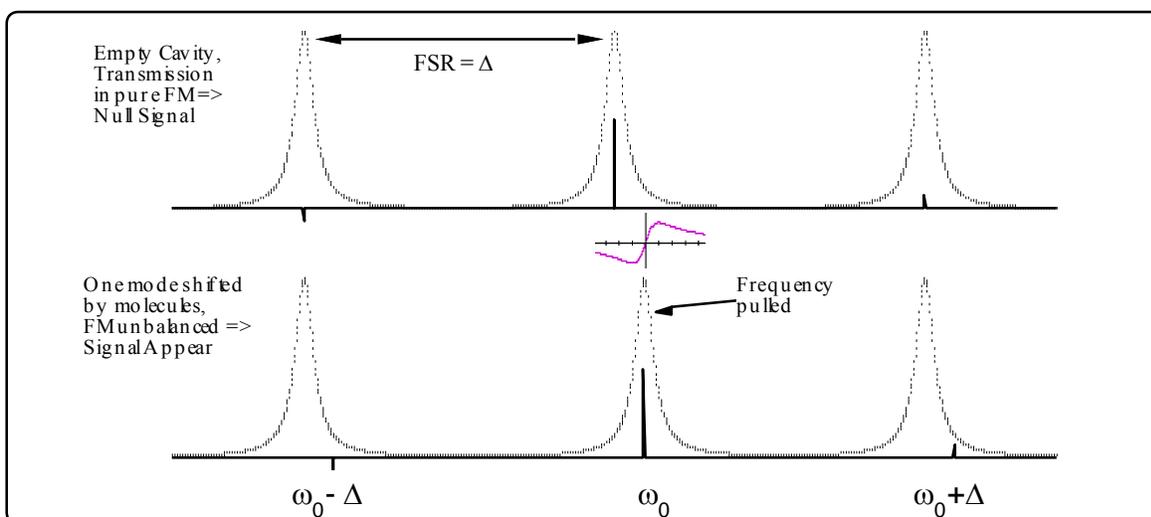


Fig 5. Basic principle of Noise-Immune Cavity-Enhanced Optical Heterodyne Molecular Spectroscopy. FM symmetry is upset when molecular dispersion shifts a cavity resonance.

Figure 5 shows the case where the central component is used to detect the intracavity molecular resonance. Initially all the FM components are lined up with their respective cavity modes.

The central cavity mode will then be frequency pulled due to the additional phase shift by the molecular dispersion. The detector viewing the transmitted light will thus generate a dispersion signal in the rf beat after the phase sensitive demodulation. We can refer to this technique as (laser frequency-) Noise-Immune Cavity-Enhanced Optical Heterodyne Molecular Spectroscopy (“NICE-OHMS”). This modulation and detection scheme enables profitable use of very high cavity finesse without any noise penalty.

**Noise immune properties** To have a convincing demonstration of the noise-immune nature of this detection, we deliberately set the laser/cavity lock to be loose and even oscillating, then we compare the recovered signal-to-noise ratios (S/N) before and after the lock was sabotaged. The result is shown in Figure 6 for the  $C_2HD$  ( $\nu_2 + 3\nu_3$ ) P(5) transition at  $1.064 \mu m$ [7]. The signals were recovered in two channels. The first one had the cavity length dithered at a low audio frequency and used a lock-in for demodulation of the direct cavity transmission (DC). The second was from the high frequency channel of NICE-OHMS. Signal lineshapes follow modulation-broadened derivatives of absorption (DC)[24] and dispersion (NICE-OHMS)[25]. The DC detection of the intracavity molecular absorption (upper row) is shown to be critically dependent upon the performance of the laser/cavity lock. (A fast, strong laser/cavity frequency-lock servo was used for the graphs in the left column,

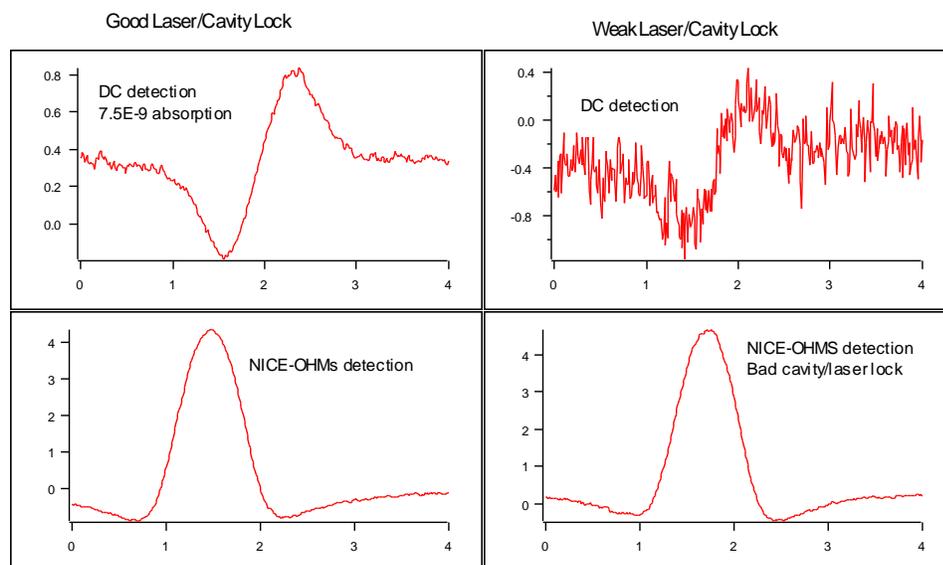


Figure 6. Demonstration of the noise-immune property of NICE-OHMS. The  $C_2HD (v_2 + 3v_3) P(5)$  resonance signal is recovered by both cavity-dither lock-in (DC) detection and NICE-OHMS technique, under conditions of a tight laser/cavity lock (left column) and a substantially deteriorated lock (right column).

while a slow and noisy servo was used for those in the right column.) However, increased laser frequency noise (relative to the cavity) yields little effect in our FM detection (bottom row).

These results were obtained in the general experimental schematic shown in Figure 7. One may use two electro-optic phase modulators to impose two sets of FM sidebands on the laser beam. The modulation at a low frequency  $\delta$  is detected in the cavity reflection signal to produce the cavity dispersion locking error for stabilizing the laser onto the cavity. Although the requirement of the laser/cavity locking is much more relaxed for NICE-OHMS than in the simple DC detection, the laser linewidth still needs to be narrowed so that a stable optical power is effectively coupled into the cavity. The sidebands at the high modulation frequency  $\Delta = \text{FSR}$  are used to probe the intracavity molecular resonances and are detected in cavity transmission, after some adequate optical isolation between the cavity and the photodiode.

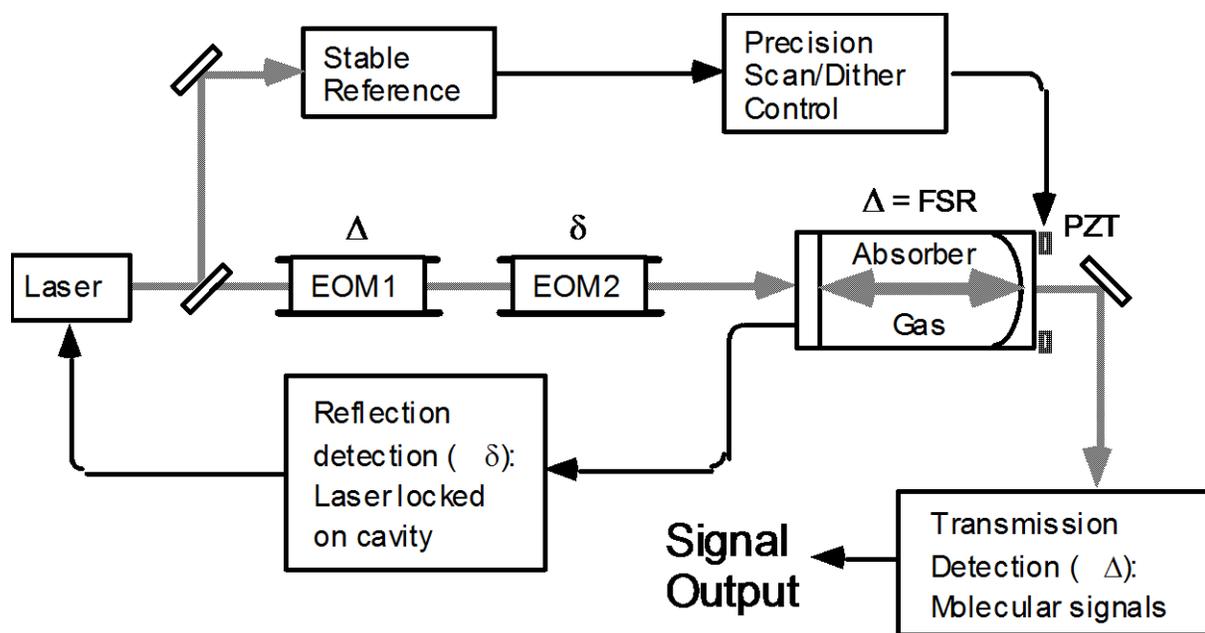


Figure 7 General experimental schematic for the NICE-OHMS spectrometer.

An important technical issue is that the recovered lineshape is influenced by a residual AM (RAM) associated with FM at the cavity FSR frequency. With an active control loop we are able to eliminate the RAM[26] and obtain a lineshape matching perfectly to a theoretical model, resulting in a flat and nearly shot-noise limited background for the fit residual throughout the entire tuning range of the resonance. A frequency offset locking loop is implemented to permit a precision sweep of the laser frequency relative to a stable reference for the study of the resonance lineshape and width. During the scan, the cavity FSR will change slightly. To maintain the noise-immune property, we actively track the sideband frequency to the cavity FSR value.

**Sensitivity statement for NICE-OHMS** Although NICE-OHMS does not bring in any extra technical noise from the laser frequency jitter relative to the cavity, it still requires carefully-maintained optical isolation throughout the beam layout to achieve the shot-noise limited performance. Compared with Equation (8) (see section III) for the ideal case of homodyne detection, the heterodyne FM suffers a factor of  $\sim 4$  loss in sensitivity for fixed total optical power. This is due in part to the power reduction implied in converting some of the main carrier to sidebands and in part to the down-conversion of shot noise from two additional spectral windows by the two sidebands. However, being able to achieve the shot-noise limit, the NICE-OHMS sensitivity is simply,

$$(\alpha L)_{\min} = \frac{\pi}{2 \cdot \text{Finesse}} \left( \frac{2Bh\nu}{\eta P_t} \right)^{1/2} \frac{\sqrt{2}}{J_0(\beta)J_1(\beta)}, \tag{9}$$

where  $J_0$  ( $J_1$ ) is the zero (first) order Bessel function with  $\beta$  being the modulation index (at FSR). A numerical example is given here for the NICE-OHMS sensitivity using our experimental parameters. Suppose  $\beta = 0.5$  and the photodiode responsivity  $\eta' = 0.85$  Amps/Watt. ( $\eta' = (e/h\nu)\eta$ ). Also assume the total detected power  $P_t = 5$  mW and the detection bandwidth =  $1/2\pi$  Hz, corresponding to a 1s time constant. Then for a plain cell, the noise-equivalent integrated absorption is:  $(\alpha L)_{\min} = 2.2 \times 10^{-8}$ . Under the same conditions, a cavity with a finesse of 100,000 improves the sensitivity to:  $(\alpha L)_{\min} = 3.5 \times 10^{-13}$ .

**NICE-OHMS method: the highest sensitivity** Figure 8 shows the experimental sensitivity we have achieved using 1.8 mTorr of  $C_2HD$  gas. The cavity finesse is 100,000 and the intracavity buildup power is  $\sim 300$  W, giving a saturation parameter of  $\sim 1.75$  and a saturation peak contrast of 13.2%. The single-pass (46.9 cm long cavity) linear absorption is about  $3 \times 10^{-8}$ . Therefore the absolute level of saturated absorption by the intracavity molecules is  $4 \times 10^{-9}$ . This is verified by the DC detection of the cavity transmission, shown in the top graph of the figure. The calibration process involves measurement of cavity finesse, on-resonance transmission, and reflection dip contrast, from which we calculate the residual round-trip cavity losses. With the laser locked tightly onto the cavity with a relative linewidth of  $\sim 1$  milliHertz, the simple cavity-dither and lock-in detection of the transmission yields a S/N (amplitude / rms noise) of 130 at 1-s averaging. This corresponds to a detection sensitivity of  $3 \times 10^{-11}$  at 1 s. The corresponding S/N from the NICE-OHMS detection is 7700 with a 1 s time constant, as shown in the bottom graph of the figure. This translates into a noise-equivalent detection sensitivity of  $5.2 \times 10^{-13}$  ( $1 \times 10^{-14}$  / cm) at 1 s averaging, about 1.5 times worse than the shot noise limit calculated previously. The NICE-OHMS result is  $\sim 60$  times better than the straightforward dither detection, basically because of its higher modulation frequency (319 MHz FM sideband frequency compared with 500 Hz dither frequency) and its insensitivity towards the laser frequency noise.

### Ultrasensitive measurement of other transitions: HCCH, HCCD, CO<sub>2</sub>

To give an indication of the extreme expansion of our spectroscopic possibilities when the detection sensitivity has increased by 5 orders of magnitude by the use of the NICE-OHMS method, we naturally seek other weak transitions within the tuning range of the Nd:YAG laser at 1.064  $\mu\text{m}$ .

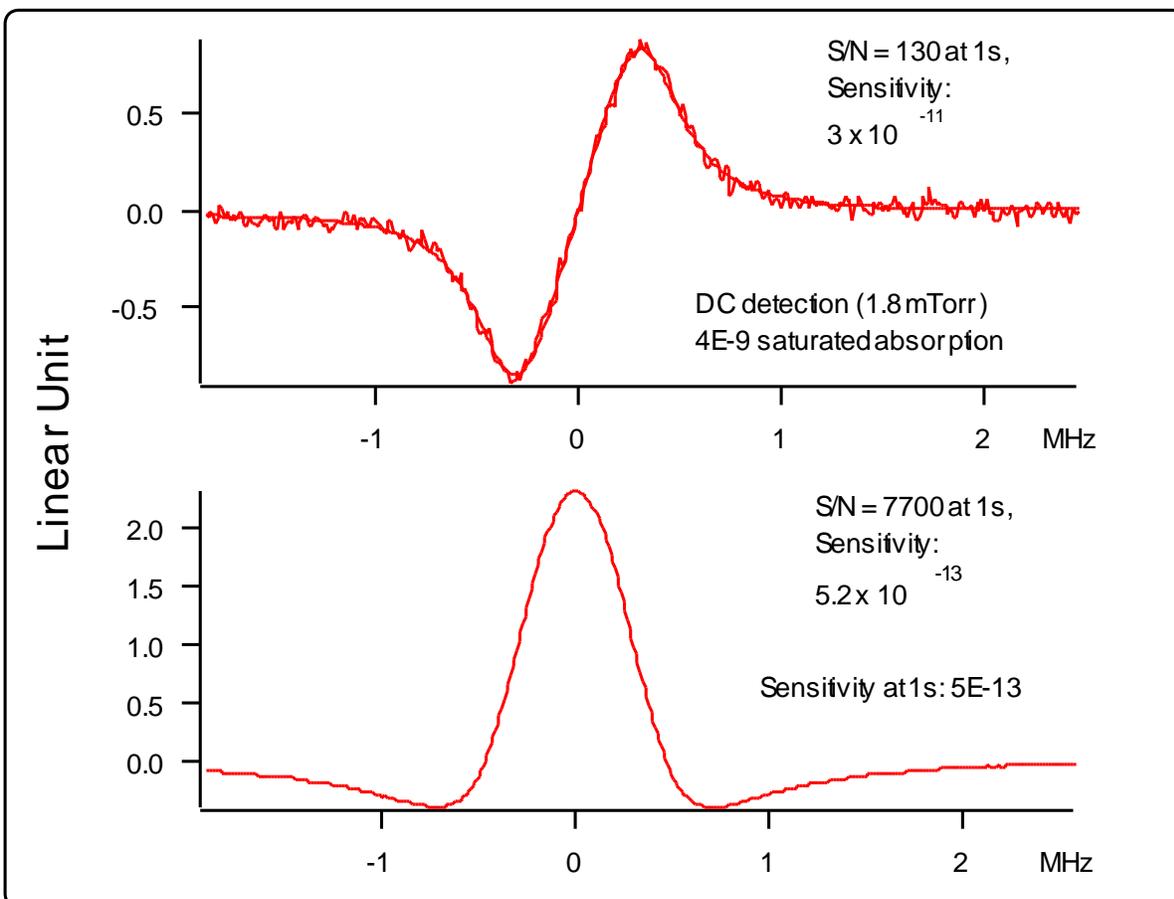


Figure 8. Sensitivity measurement of the NICE-OHMS technique. The upper graph shows the level of the saturated absorption while the lower graph shows the corresponding S/N obtained via NICE-OHMS. The noise equivalent detection sensitivities (normalized to 1s time constant) are  $3 \times 10^{-11}$  for cavity dither detection and  $5.2 \times 10^{-13}$  for NICE-OHMS.

We have measured two such additional lines, namely  $^{12}\text{C}_2\text{H}_2$  ( $2\nu_1 + \nu_2 + \nu_5$ ) R(12) [27] and  $^{12}\text{C}^{16}\text{O}_2$  ( $2\nu_1 + 3\nu_3$ ) R(6), [28] with their respective transition dipole moment of 50  $\mu\text{Debye}$  and 6  $\mu\text{Debye}$ . (1 Debye =  $3.33564 \times 10^{-30} \text{ C} \cdot \text{m}$ ) They are both weaker than the  $\text{C}_2\text{HD}$  ( $\nu_2 + 3\nu_3$ ) P(5) transition, which has a transition dipole moment of  $\sim 70 \mu\text{Debye}$ .

Using the same gas pressure, optical power, and cavity dither amplitude, we compare the saturated absorption signals of  $\text{CO}_2$ ,  $\text{C}_2\text{HD}$  and  $\text{C}_2\text{H}_2$  in Figure 9. The  $\text{C}_2\text{H}_2$  transition is recovered with an excellent signal-to-noise ratio, as shown in Figure 9 (c). The signal size is about 1/4 of that for  $\text{C}_2\text{HD}$ , using the same gas pressure and optical power. It provides another frequency reference for the Nd:YAG laser, besides  $\text{C}_2\text{HD}$ . The center frequency of the resonance is 281,612,403.278 (.025) MHz, i.e., it is 17708.458 (.014) MHz red of a frequency doubled

Nd:YAG laser locked on the  $a_{10}$  hyperfine-structure component of the R(56) 32-0  $I_2$  transition.[29] The pressure broadening rate of 34(1) MHz/Torr (FWHM) is similar to that of  $C_2HD$ . [7]

For the  $CO_2$  transition, however, the saturated absorption signal is much weaker than the  $C_2HD$  line, by more than a factor of 350. This  $CO_2$  resonance involves two quanta of symmetric stretch and three quanta of antisymmetric stretch of the C-O bond.[28] The bending mode ( $\nu_2$ ) is not excited. The life time of the excited vibrational state is estimated to be  $\sim 2$  ms, mainly due to the IR fluorescence on the vibrational transition  $(2, 0^0, 3) \Pi (2, 0^0, 2)$ . The relevant molecular constants are ( $cm^{-1}$ ):  $B' = 0.39021894$ ,  $D' = 1.33373 \times 10^{-7}$  for the ground state, and  $B'' = 0.38234$ ,  $D'' = 1.71$  for the excited state with the band origin at 9388.990.[30]

Under exactly the same experimental conditions (except for the change of sample gas), the recovered lineshape associated with the  $^{12}C^{16}O_2 (2\nu_1 + 3\nu_3)$  R(6) transition is vastly different from either  $C_2HD$  or  $C_2H_2$ , as indicated in Figure 9.

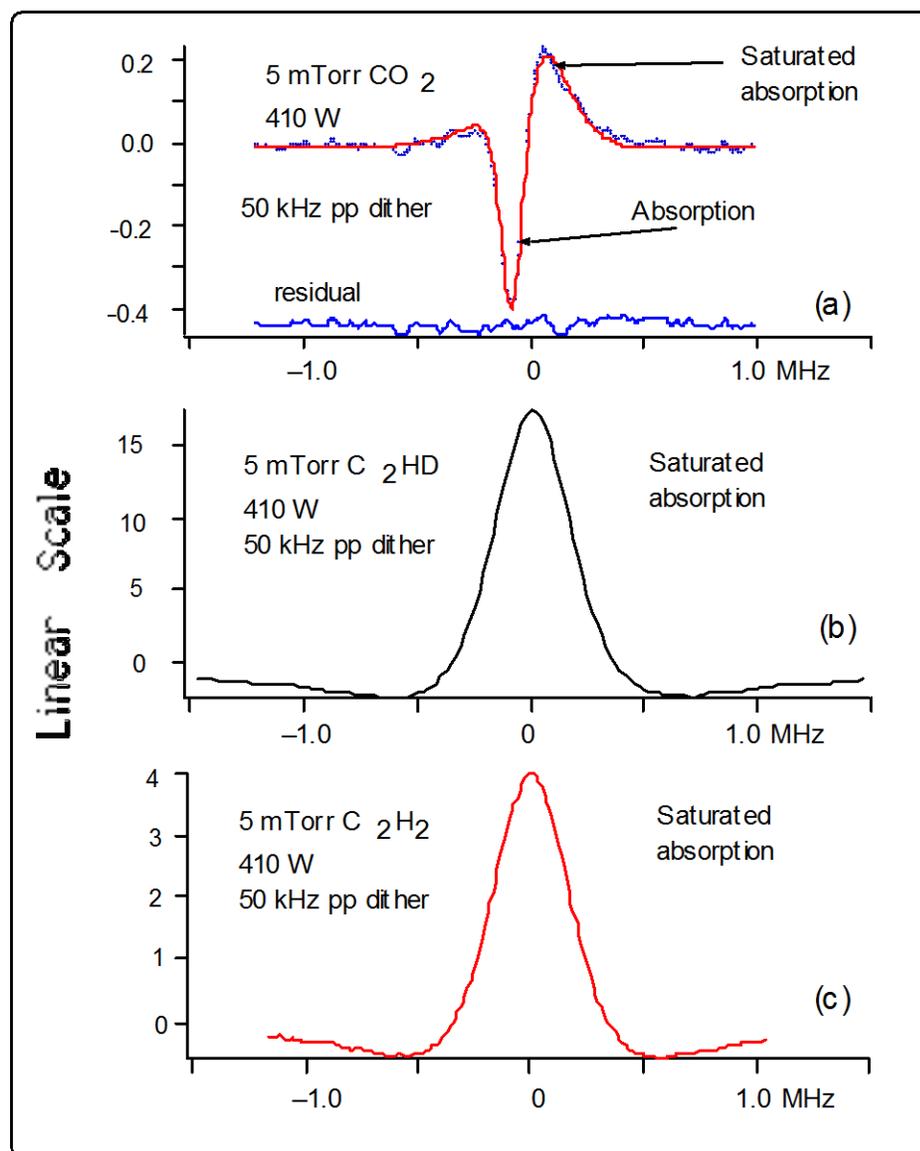


Figure 9. Lineshape comparison among the resonances of three molecules. (a)  $CO_2$ , (b)  $C_2HD$ , and (c)  $C_2H_2$ , all data taken under the same experimental conditions. The negative-going  $CO_2$  resonance has a zero-pressure extrapolated linewidth of  $\sim 100$  kHz, half the value of the transit-time broadening. These aspects lead us to tentatively identify this feature as arising from two-photon absorption.

## VI. Laser stabilization by NICE-OHMS

In the work of optical frequency metrology, the NICE-OHMS technique can provide us with thousands of weak molecular lines as high quality visible frequency/wavelength references. The narrow linewidths associated with these molecular transitions are invaluable, as they facilitate better definitions of the linecenters to ensure long-term stabilities. Using the NICE-OHMS method, the high signal-to-noise ratio of the resonance information helps to reach the desired short-term stability in reduced averaging time, permitting more effective intercomparisons among various frequency standards. With the narrower linewidth - but lower S/N - of the C<sub>2</sub>HD overtone transition, we have currently achieved a level of stability similar to that of the I<sub>2</sub> system[29]. However, the long natural lifetime of overtone transitions provides the opportunity for optical selection of slow molecules to produce a much narrower linewidth (currently by 13 times) than the room temperature transit time limit. (Slow molecules are the ones preferentially responding when the power and pressure are very low.) The narrower line should further improve the long term stability and reproducibility.

A very effective representation of the frequency noise in the time domain is by the Allan variance.[31] In calculating the Allan variance one simply compares adjacent frequency measurements and then averages this difference over the whole data set. The time interval between the adjacent measurements is basically the averaging time for the frequency noise. The Allan variance permits one to separate and isolate different noise processes based on their time scales. In the short-time domain, the Allan variance typically displays a slope of  $\tau^{-1/2}$ , where  $\tau$  is the averaging time. This is because the main contribution to the fast noise originates from white noise, ideally, the shot noise. One thus sees from this argument that the level of this short-term variance is fixed by the ratio between the frequency discrimination linewidth and its S/N. Figure 10 also shows the calculated Allan variance from the beat record of the two stabilized lasers. The variance is normalized to the optical carrier frequency, i.e., 282 THz (1.064  $\mu\text{m}$ ). The Allan variance of  $\sigma_y = 2 \times 10^{-13}/\sqrt{\tau}$  improves to  $6 \times 10^{-15}$  at a longer integration time ( $> 1000$  s), a promising indicator for an ultrastable frequency reference.

This amazing frequency stability achieved by the extremely weak reference transition is a direct result of our spectrometer's ultra-high detection sensitivity. Notice that the C<sub>2</sub>HD-stabilized system shows only 2 - 4 times more noise than the I<sub>2</sub> system, a remarkable success considering the green I<sub>2</sub> transition strength is almost a million times stronger than the P(5) line of the C<sub>2</sub>HD ( $\nu_2 + 3 \nu_3$ )

overtone band. The short-term frequency stabilities of the optical sources are comparable to or

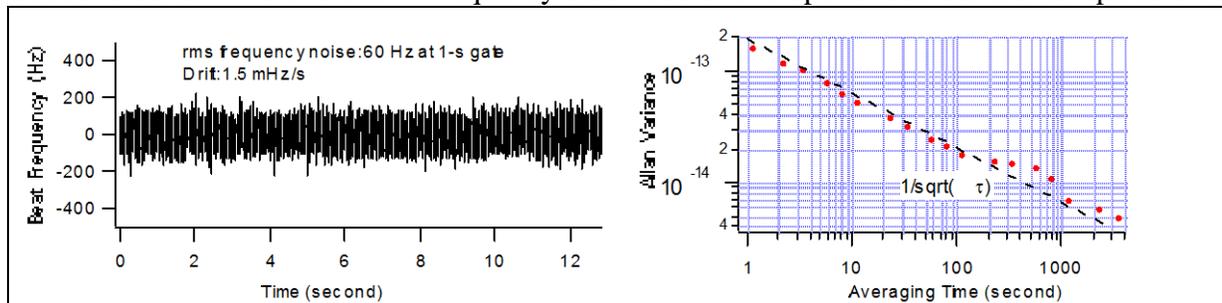


Figure 10a. Stability of beat between I<sub>2</sub> stabilized and HCCD-stabilized lasers. The improving ultrasensitive detection of a weak overtone resonance of molecular HCCD permits progressively better results on the laser stabilization. The heterodyne reference laser is stabilized on an I<sub>2</sub> transition at 532 nm using modulation transfer spectroscopy. This reference laser has a stability  $\sim 5 \times 10^{-14}$  at 1 s, from beating experiments with two I<sub>2</sub>-stabilized systems. See Fig 10b.

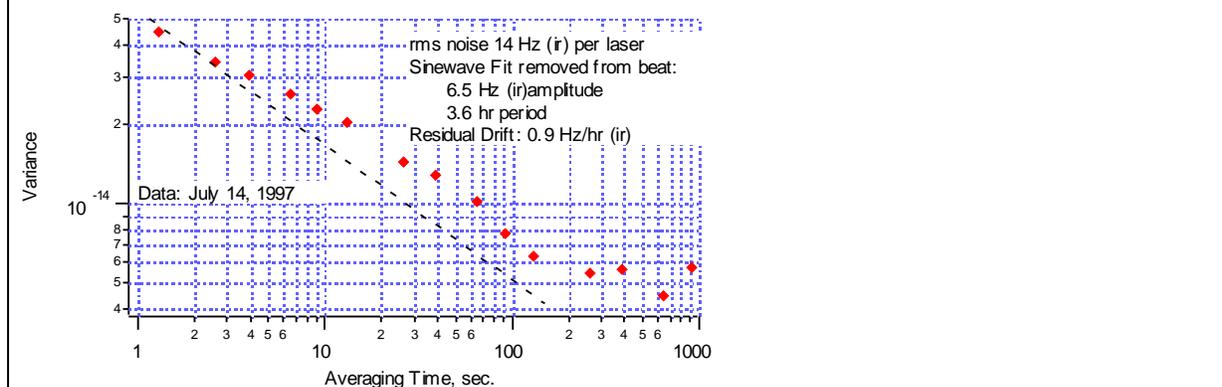


Figure 10b. Stability of beat between two I<sub>2</sub>-stabilized lasers, using R(56) 32-0 transition, a<sub>10</sub> hyperfine component and modulation transfer spectroscopy. We note that the molecular absorption is nearly a million-fold stronger than that of the HCCD used for Fig 10a, above, but the stabilization results differ by a mere factor of 4 !

better than the state of the art microwave standards. However, the optical reproducibility and accuracy are not yet comparable. The urgent task is therefore to vastly reduce the systematic influences on the optical transition line-centers.

Our NICE-OHMS spectrometer naturally provides laser frequency discrimination information by both the cavity resonance and the molecular transition. It is thus an ideal system for achieving simultaneously good short- and long-term frequency stabilizations. The laser frequency basically tracks the cavity resonance on the level of a few milliHertz with a fast servo loop. The vibration noise and the long-term drift of the cavity can be reduced - or basically eliminated - by stabilizing to the intracavity molecular transition.

The NICE-OHMS signal is intrinsically dispersive when the molecular resonance is probed by the carrier of the FM triplet. However, in practice we found it necessary to dither the cavity length and make a 2-nd derivative signal recovery of the rf balanced mixer signal output. In part this can suppress the baseline offset problem associated with the imperfect FM modulation at the FSR frequency. However, to achieve the best stabilization results, it is crucial that the FM has a zero (or at worst a small constant) residual AM so that the pure FM dispersion signal lineshape is not contaminated by the absorptive phase component. Active control of the modulator was used in our setup.[26]

To summarize, we checked the quality of this overtone-stabilized laser at 1.064 μm against a frequency-doubled Nd:YAG / I<sub>2</sub> reference system via optical heterodyne beat. (The 532 nm-

stabilized laser has a stability  $\sim 5 \times 10^{-14}$  at 1 s, from beating experiments with two I<sub>2</sub>-stabilized systems.) In Figure 10 the counted beat frequency vs. time shows a drift  $\sim 5$  Hz/h and a 60 Hz frequency noise at 1-s counter gate time, in direct agreement with the S/N available at 1.064  $\mu\text{m}$ .

## VII. General Concluding Advice/remarks on attaining the highest sensitivity

It is clear that some dramatic progress in optical detection sensitivity is possible if we can learn well how to separate the molecular signal from the cavity's stored field, and perform the detection at a frequency where there is no non-fundamental noise to bother us. Basically we have to determine the cavity's response simultaneously for the on-resonance and off-resonance cases, so they can be subtracted to reveal the molecular absorption of interest. We have explained how the FM method of NICE-OHMS works to implement this signal isolation and subtraction continuously and simultaneously in real time, and we have illustrated the unprecedented sensitivity level of  $5.2 \times 10^{-13}$  integrated absorption. Still, we feel there may be some repetitive transient heterodyne detection scheme which will also satisfy our design principles for good sensitivity, ideally with lowered technical requirements for the laser system. However even if this dream is not immediately realizable, it is in fact rather straightforward to perform the laser stabilization and modulations at the level required for NICE-OHMS. One must see there is a vast difference between doing the laser stabilization for the first time and doing it again: we are ready to work with the interested community to help this sensitivity be more widely available to interested spectroscopists. Some technical "how-to-do-it" workshop(s) and publications are foreseen for the near future.

## VIII. Acknowledgments

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