Review of methods for improving sensitivity in field systems
Robert Curl
Department of Chemistry
Rice University

FLAIR, September 13, 2016

The material in this talk will be mostly be well-known to this audience. I’ve found that reviewing the subject after a long break turned out to be highly educational for me. I hope you will find some things to think about here.
Atmospheric monitoring is by two approaches. One can either flow the atmosphere through a cell where you can control conditions of temperature and pressure. Or on can send a laser beam through the atmosphere and detect the changes in the beam by comparing the signal from a detector located near the source with one observing the beam after it passes through the atmosphere.

**Two basic approaches**

- **Point measurements**
  - **Advantages**
    - Control of conditions of measurement
    - More methods available to improve S/N
- **Open path measurements**
  - **Advantages**
    - Can directly measure average concentrations over long paths outdoors
    - Sometimes very long path lengths can be used
The object, of course, is to determine the concentration of the species of interest. In order to do this, one must be sure that the observation is not contaminated by signals from other species, and one must be able to measure the signal from the molecule of interest. To do this sensitivity must be adequate and one must know the conditions under which the measurement is made.

The main concerns

- Interference from other species present
  - Usually present for any large molecule
- Sensitivity issues
  - High frequency noise
  - Baseline flatness and stability
- For high relative accuracy, precise pressure and temperature control required
In general, only a few species can be monitored through their electronic transitions because a large fraction are dissociated by ultraviolet light. Because so many species dissociate and therefore have broad spectra and their concentrations in the atmosphere vary, only very light species have rotationally resolvable spectra at atmospheric pressure. Fluorescence detection is potentially the most specific and the most sensitive, but is quenched by collisions with other molecules.

Infrared is the true workhorse of atmospheric monitoring simply because such a large fraction of target molecules have good transitions for absorption detection in the mid-IR.

Most molecules have rotational transitions potentially useful for atmospheric monitoring. However, any transitions at 2 cm⁻¹ and below produce weak absorption because of the competition between absorption and stimulated emission. In addition, the energy per photon is small creating small current signals upon rectification. In the higher frequency region above about 8 cm⁻¹, absorption by H₂O rotational transitions makes the atmosphere almost opaque. In addition, the population of the lower level of transitions for larger molecules is greatly reduced because transition frequencies grow as J while energies grow as J(J+1). The region around 3 cm⁻¹ offers the best hope for monitoring molecules like NO and CO, but their vibrational transitions near 2000 cm⁻¹ provide better monitoring opportunity.
These are all species of importance in atmospheric chemistry, but they are reactive free radicals making it difficult to be certain that the concentration reaching a cell is the same as the concentration in the atmosphere. Fluorescence is quenched around atmospheric pressure although as long ago as 1975 workers at Ford Motors reported detecting OH fluorescence in the GM parking lot even though the fluorescence quantum yields were less than 1%.

Terry Miller’s group has investigated the near UV spectrum of a variety oxy alkyls in fluorescence without observing these species atmospherically. Likewise his group as investigate several peroxy radicals in the near IR using cavity ringdown.

**Suitable Electronic Transitions**
(possible examples)

- Fluorescence
  - OH
  - Oxy Alkyls (CH\(_3\)O, RO)
- Absorption*
  - Peroxy Alkyls (CH\(_3\)O\(_2\), RO\(_2\))

\*Near IR cavity ringdown
The integrated intensity of a rotational component of a vibrational transition, i.e. its linestrength depends only upon concentration and temperature. Many of these for species of interest have been tabulated in the HITRAN database readily accessible to all.

For an isolated rotational component, starting at low pressures the peak absorption grows with increasing pressure until pressure broadening out competes Doppler broadening at which higher pressure merely broadens the line. Thus most cell monitoring of light molecules is usually done at about 100 mbar or less.

As you well know, the apparatus and methods used for cell monitoring are far more complex than this, and a number of problems must be overcome in order to obtain good concentration results.
I will discussing issues of overlapping lines next. Most of the time, the species of interest is present in very low concentration so that is difficult to discern its absorption from a rolling baseline. These are often caused by accidental etalons, which have an annoying habit of shifting with time. Any such etalons that have peak to valley frequency difference comparable to the width of the absorption line being monitored present a particularly nasty problem in obtaining accurate results for trace species.

There is always noise present. The most fundamental is the “white noise” arising from the intrinsic nature of photons and electrons. The power spectrum of such white noise is flat. In addition there is always “technical noise”, which arises from several sources and, in contrast to “white noise” these are given names like “pink noise equals “flicker noise equals “1/f noise”.

It’s not that simple

- Overlapping lines
- Baseline problems
  - Unstable
  - Rolling
- Noise
  - White noise
  - Technical noise
The atmosphere has many species particularly water and carbon dioxide that absorb strongly in the IR. If one wishes to measure the concentration of a trace species, the spectral region of interest must be searched to find regions where weak lines of abundant species and even moderate lines of less abundant species do not interfere.

In general, the rotational structure of vibrational lines of larger molecules usually cannot be resolved even at the Doppler broadening limit. When this becomes a problem is typically determined by how many low lying rotational and vibrational states and by the frequency of monitoring since the Doppler width is proportional to frequency. Thus in the 1 cm\(^{-1}\) region rotational spectra of quite large molecules can be resolved as long as they are sufficiently volatile. On the other hand, at over 3000 cm\(^{-1}\) the rotational structure of a molecule as CH\(_3\)OH is not really resolvable exhibiting some indications of rotational structure but not the extent that such structure can be used for monitoring.

The whole field of chemometrics is aimed at solving the problem of different species with overlapping absorptions by using linear combinations of several absorptions at different wavelengths.

There is a chance that infrared-infrared double resonance might useful in isolating signals of a single molecule even in the case of overlapped rotational structures, but quantitative use remains problematical.
Sensitivity is determined by S/N

To improve it one can either increase signal or reduce noise.
In multipass absorption cells, the light beam is bounced off mirrors. Although cells have been constructed with more than two mirrors, these tend to impractical. Two issues arise tending to limit the pathlength obtainable with multipass cells. The first is that there is power loss with each reflection. This is rarely a problem with laser sources. The other is that, particularly in older designs, the number of reflection spots on the mirrors is limited by the overlap of spots. Overlapping spots create an etalon and often with resonance frequencies in the range of 50 to 150 MHz, which is comparable to the Doppler line width around 2000 cm\(^{-1}\). This is exactly the wrong kind interference for the quantitative measurement of weak gas phase absorptions making it difficult distinguish absorption from etalon, and the frequencies of the etalon peaks tend to drift. The older Herriott and White cells used only a small portion of the mirrors. You can solve this problem by using a very long, large mirror cell, but generally it’s difficult to find space for one, and large mirrors cost. About a decade ago Areodyne started selling astigmatic multipass cells that use the whole area of the mirrors. More recently one of Franks former students Stephen So came up with a new design.

Another way to obtain long pathlengths is by using optical cavities. One can either measure transmission through the cavity or one can measure ringdown. Using mirrors of very high reflectivity, a light pulse can bounce around in such a cavity for up to a millisecond corresponding to tens of kilometers of pathlength. An advantage of this is that the ringdown measurement is made when the laser is turned off so that laser power fluctuations become irrelevant. Acoustic resonant structures are also used to increase the acoustic signal in photoacoustic spectroscopy.

### Signal enhancement measures

- If observing the decrease in power of the laser beam, increase molecular absorption by increasing path length.
  - Multipass cells
  - Optical cavity ringdown or absorption
- In photoacoustic spectroscopy, use acoustically resonant structures.
As mentioned earlier, “white noise” with a flat power spectrum is intrinsic to the particulate nature of photons and electrons. It is susceptible to reduction by time integration. The graph shows the variance of white noise decreasing as the reciprocal of integration time. S/N actually is proportional to the root of time because it is the std deviation of the noise in the denominator. In the graph above, technical noise begins to be significant at integration times of 20 sec.

Since the noise in the figure is intrinsic in one way or another is there any way to improve S/N. In high sensitivity laser absorption spectroscopy, the signal is just a tiny decrease in the laser carrier and the carrier intrinsically contains the noise. If we have some way of separating the signal itself from the noise, the intrinsic noise of the signal is much smaller.

Other very low frequency noise sources can often be equated to “drift”, but in some cases it can be a sudden shift in baseline caused by some environmental change. With long term integration, this can look like drift, but can be detected as different from drift by closer examination of the data being integrated.
The best that can be done is to use the heterodyne technique. If one has some means of modulating the amplitude of the signal separately from the carrier, then the signal is found in the sidebands on the carrier signal. When the laser power is detected, the detected signal is proportional to the power, but the signal sidebands correspond to the modulation of the laser electric field and the electric field is squared upon detection. Thus a modulation in the detector current proportional to the product of the carrier voltage with the signal voltage is developed.

Back in 1973 Koichi Shimoda worked out what the resulting limiting sensitivity would be. In the case above, for a 1 mW laser, a change in power of about one part in $10^7$ would be at the threshold of detection.

Limit of heterodyne absorption spectroscopy

This issue was addressed by Koichi Shimoda in 1973. *Applied Physics* 1, 77-86 (1973)

In heterodyne detection, a local oscillator offset in frequency is mixed with the signal on the detector. The beat signal gains because the optical voltages are being detected.

$$P - \Delta P = k (V - \Delta V)^2 = k V^2 - 2 k V \Delta V + k (\Delta V^2)$$

Thus

$$\Delta P_{\text{min}} = 2 k V \Delta V = \sqrt{16 P_n P}$$

where in the mid-IR $P_n = h \nu B / \eta$

$B$ is the bandwidth and $\eta$ is the quantum efficiency of the detector.

For $\eta = 0.2, \lambda = 5 \mu, B = 1 \text{ Hz}, P = 1 \text{ mW}, \Delta P_{\text{min}} = 8 \times 10^{-11} \text{ W}$. 
Unless the laser power is very small, i.e. detector noise limited, S/N can never be improved by amplitude modulating the laser.

Reason: Any noise (white, technical or baseline rolling) in the laser, is translated to the modulation frequency.
For heterodyne detection, we need some means for turning the absorption on and off or at least changing its size. The techniques listed under modulation of the absorption can help do this. Each has its advantages and limitations, and they need to be discussed separately.

Photoacoustic spectroscopy is not a heterodyne method, but does aim to separate the signal from the carrier and thus sort of belongs in the same class.
The simplest version of this experiment is scanning over the line, fitting the background with sample absent and subtracting it. By harmonic analysis, one can make the line contrast more. In doing this the line contour is used whether measured or assumed.

Often the S/N is limited by accidental etalons with FSR similar in magnitude to the line width that drift in time because of small changes in temperature and even atmospheric pressure.
Using an electro-optic modulator, one can impose a modulation upon a laser beam that is, in theory, a pure phase modulation. In first order this is equivalent to frequency modulation. When one of the sidebands is on the line and the other is not, phase modulation is converted to amplitude modulation.

**Phase Modulation**

1. PM frequency has to be comparable to the line width. In the mid-IR, Doppler linewidths are ~100 MHz.* Fast detector needed.†

2. It tends to be difficult to avoid residual amplitude modulation, which limits S/N. A feedback loop (requires fast detector) can remove this.

*FM, not PM, is widely used for spectroscopy near 30 cm⁻¹.
†One can use tone modulation to get round this.
It is challenging to come up with a scheme for frequency modulating a laser by putting a frequency modulation sideband that contains only a carrier and two symmetrically placed sidebands.

It is much easier to phase modulate a laser beam using the Pockel’s effect. The resulting laser electric field is shown here. It is not the ideal frequency modulation. Instead an infinite number of sidebands are produced. In the formula, $z$ determines the modulation index.

Note that $|E|$ can never be larger than $E_0$ because $\pm 1$ is the range of $\cos$. Thus power is conserved regardless of $z$.  

Phase modulation

Use Electro-optic modulator to obtain a electric field of the form:

$$E = E_0 \cos \left( \omega_0 t + z \cos \left( \omega_Mt \right) \right)$$

By using the Jacobi-Anger expansions of

$$\cos[z\cos(x)] \& \sin[z\cos(x)]$$

the structure of the modulation sidebands can be determined.
The sideband structure for the reasonable modulation index of 0.5 is depicted. In the experiment, the beat note of $\omega_M$ between the zeroth order band $\omega_0$ and the + and – first order side bands is the prime interest. In the absence of absorption, the phase difference between these two beats is $180^0$ and thus they cancel. If one band is absorbed more strongly than the other, the cancelation is reduced and a signal at the modulation frequency results.

In the expansion that gives rise to this structure, the amplitude of a side band with index $m$ is given by $J_m(z)$ where $J$ is the Bessel function.

If you crank up the modulation $z$, the structure becomes complicated.
It is often difficult to find a detector with a response time small enough to support phase modulation frequencies large enough in comparison with an absorption line profile.

If one has a fast phase modulation frequency giving a significant change in absorption signal, one can match a slower detector by turning the phase modulation frequency on and off. Then detect at this lower tone frequency.
Sometimes one is interested in monitoring a paramagnetic molecule. For example in urban smog monitoring two of the components of NOx, NO and NO$_2$, magnetic rotation, or Faraday rotation, if you like, can provide great improvement in sensitivity for these species.

### Magnetic Rotation

- Limited to rotationally resolvable paramagnetic molecules, e.g. NO, NO$_2$
- Depends upon the rotation of polarization by a magnetic field in the direction of propagation
- Detects dispersion rather than absorption
- Using an oscillating magnetic field between two nearly crossed polarizers, a signal is created with greatly reduced technical noise from the laser.
- For quiet lasers, splitting the beam into two 45° polarizations and observing the difference between two detectors can provide larger signals as long as detector saturation is avoided.
Here is an example from Frank Tittel’s lab of work by Gerard Wysocki giving sub ppbv sensitivity.
This study by Gerard shows how important it can be to isolate the signal from background in overcoming long term noise.
The NICE-OHMS technique combines *cavity enhanced absorption spectrometry* (CEAS) for prolonged interaction length with the sample with *frequency modulation* (fm) spectrometry FMS for reduction of *1/f noise*. By choosing the fm-modulation frequency equal to the *free spectral range* (FSR) of the cavity, all components of the spectral fm-triplet are transmitted through the cavity in an identical manner. Therefore the cavity does not compromise the balance of the fm-triplet, which otherwise would give rise to fm-background signals. It also does not convert any fluctuations of the laser frequency with respect to the transmission mode of the cavity to intensity modulation, which would deteriorate the detectability by the introduction of intensity noise. This is referred to as "noise immunity". All this implies that FMS can be performed as if the cavity were not present, yet fully benefiting from the prolonged interaction length.
I show you a simple version of the NICE-OHMS experimental arrangement in order to point out that like phase modulation it uses EOMs. Thus while the typical discussion of NICE-OHMS is in terms of just the two first order side bands, there are others present.

nuM is set to the mode spacing the cavity, while nuPHM is much smaller and is used to lock laser to cavity.
In this method, two laser beams derived from the same source are passed through the cell without absorber with their optical pathlengths through the cell adjusted to minimize the 50 MHz signal. Introducing sample and scanning the laser over the absorption line approximately produces the derivative of the dispersion giving a lineshape like the magnetic rotation signal you’ve already seen. This appears as phase modulation of the signal at 50 MHz. Gerard and Damien prefer to think of this as a frequency signal. I don’t because as we’ve seen even a pure frequency phase modulation produces many frequency components. In terms of S/N this system has many of the properties of wavelength modulation. However, it is far less sensitive fluctuations affecting both frequencies because it divides one lock-in phase by another. . Up to a point S/N is improved by increasing the scan repetition rate because of more averaging. However, any wavelength dependent signals with lineshapes of the same frequency range as the line being monitored do not average out.
A very significant advantage of CLaDS is that the signal depends upon the difference in the experience of two beams with a small frequency separation following essentially identical paths. Through phase detecting both in-phase and out-of-phase signal, and taking their ratio background is flat and propagation effects cancel. This can be tremendous advantage for open path monitoring in that they beams should experience the same atmospheric fluctuations.
Finally here is an overview of estimated sensitivities of various absorption methodologies. Note that sensitivity is enhanced about a billion fold over direct absorption and about a million fold over wavelength modulation.
Finally we consider photoacoustic spectroscopy as a means for separating signal from background thereby improving sensitivity.

This really old pre-laser technology has proved a useful way to use lasers.

This is the cartoon.
This is reality.

Figure 4 Resonant photoacoustic cell.

1, resonator;
2, buffer volume (maximum diameter 40 mm, length 50 mm);
3, buffer ring to decrease buffer radius;
4, ZnSe Brewster window;
5, adjustable l/4 notch filter to suppress window signal;
6, inlet gas flow;
7, l/2 notch filter to suppress flow noise;
8, outlet gas flow;
9, microphone.
I won’t dwell upon this approach because the rest of the talks are likely to do that. It was an idea put forth by Anatoliy Kosterev when he was in Frank’s group. It has turned out to be a very good idea. It turns out that one can get performance in a compact system using cheap tuning forks rivaling the performance the best resonant cell systems.
Wavelength modulation

When absorption lines are narrow in frequency compared to variations in power reaching the detector, S/N can be improved by repeatedly scanning the laser across the line and detecting at a harmonic of the scan frequency.

The aim is to suppress the first (or occasionally the second) derivative of the power variation thereby partially separating the signal from the carrier.

Typically there are significant variations in power reaching the detector arising from accidental etalons involving reflections off-surfaces. These often result in power variations comparable in scale to the molecular line.

Window reflections can be suppressed by cell Brewster windows, but usually extreme care must be taken to avoid accidental etalons involving reflections from source, detectors, and other optical elements.

If the laser power does not change in the modulation and there are no etalons in the beam path, then the white shot noise limitation is determined by Shimoda’s heterodyne limitation. However, the “accidental etalon” limitations hold as might be expected.
I imagine everyone here is familiar with the Voigt profile in absorption and also knows of the intimate connection between absorption and dispersion. But fewer may be familiar with how to include the combination of pressure broadening and Doppler broadening in dispersion. These interlocked quantities are combined into the function $Z$ which is known as the plasma dispersion function even though at least one book has been written about it.

The complex light propagation constant of a Doppler/Pressure broadened line is

$$k(v) = \frac{\lambda S}{u \sqrt{\pi}} Z \left( \left( v - v_0 + i \Delta \right) \frac{\lambda}{u} \right)$$

The imaginary part of $k$ is the absorption coefficient and the real part is the dispersion.

$S$ is the integrated line intensity tabulated in HITRAN. $u = \sqrt{\frac{2k}{m}} - \Delta$ where $k$ has dimensions of $1/\text{length}$, $S$ of time, $Z$ dimensionless, $\nu$ of $1/\text{time}$, $\Delta$ $1/\text{time}$, the argument of $Z$ is dimensionless since $\lambda u$ has dimension of time.

$Z(x)$ is the plasma dispersion function

$$Z(x) = 2i e^{-x^2} \int_{-\infty}^{ix} e^{-t^2} dt = i \sqrt{\pi} e^{-x^2} \left[ 1 + \text{erf}(ix) \right] = i \sqrt{\pi} e^{-x^2} \text{erfc}(-ix)$$

The version of *Mathematica* I use does not have $Z$ defined, but it does have both erf and erfc for complex arguments.
Interaction between uncrossing angle, signal, and noise

A: Signal
Linear in angle

B: Noise
Quadratic in angle

C: S/N

The noise at small $\alpha$ is a combination of laser noise from polarizer leakage and/or detector noise.
Stark modulation

The splitting of M degeneracy by an electric field provides a means for creating an AC absorption signal suitable for heterodyne detection. This is the workhorse approach to microwave spectroscopy at frequencies below 2 cm\(^{-1}\) where operating pressures are <100 mTorr.

No one has found a way to make this work in the mid-IR because the fields required to split M degeneracy* by the line width cause electric discharge in the sample.

*Exception: Some molecules have fast first order Stark effect.
NICE-OHMS example

(a) frequency modulated
(b) wavelength modulated
Doppler-broadened NICE-OHMS signals from 13 ppb of C$_2$H$_2$.

Ove Axner, Unpublished figure, Wikipedia