Advanced Measurement Techniques in Fluid Mechanics and Heat Transfer

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Week – 11
Lecture - 54
Tunable Diode Laser Absorption Spectroscopy – 2

Okay, in this class, we are going to do the second part of TDLS, which will look into how TDLS evolved as a measurement technique. So we are going to this particular page, which starts with the Beer Law and the Line Shapes. All right, so let's go into presentation mode. Okay, so in the Beer-Lambert law and line shapes. So imagine that this is a system with dimensions of one meter by one meter in L, and there is an incident radiation $I_o = Fhv$, where F is nothing but the intensity of the flux of photons, basically, which is impinging on the left-hand side. And it is coming out of the right-hand side after passing through this particular system.

So the intensity of the beam that is coming out of the system on the right face is attenuated or enhanced depending on the relative dominance of stimulated absorption or emission. So if there is absorption, this will go down. When there is an emission, then this will get added, and this will increase. Neglecting spontaneous emission in the process, the two-level rate equation, if you recall, is given as follows, because spontaneous emission is neglected.

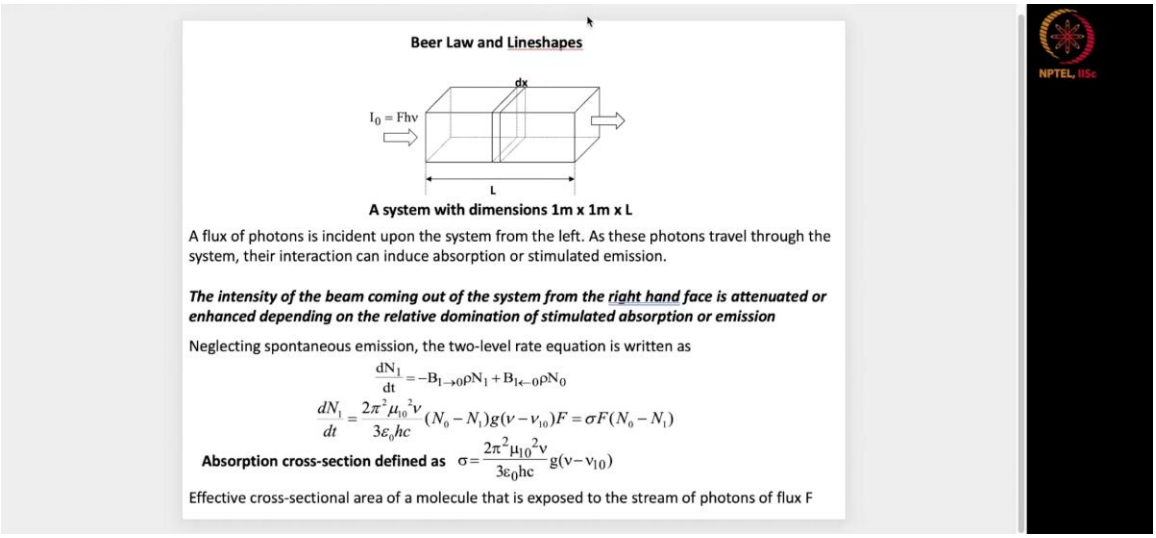
So this is dN_1/dt. So, that is the population increase in the higher energy level. And if we now place the expressions for b and the two b's, basically you get that this is multiplied by 2; therefore, this gets you h, which is the line shape function into f. In other words, if you pack everything, all these factors, which is 2π squared up to this, you can represent it by sigma, and this is f into n naught minus n1. Right.

So you can see that this sigma is therefore called the absorption cross section. It's the effective cross-sectional area of a molecule that is exposed to a stream of photons with flux F. This is where it exactly comes from. Right, so the flux is incident on the left of a small element of thickness tx with a unit cross-sectional area. Then, the change in flux that is caused by passing through an element of dx is given by $-\sigma F(N_0 - N_1)dx$

If we integrate it over the entire path length l, we get this: that means F/F_0. F is the flux that is coming out, and F_0 is the initial flux that was entering, which is given as the intensity I/I_0, expressed as the exponential of $-\sigma(N_0 - N_1)l$. In other words, we can

write it as $-KNl$. This entire expression is called Beer's law. For absorption spectroscopy, Beer's law relates the attenuation of the intensity of the incident light to the molar absorption coefficient and the concentration of species.

So, the molar absorption coefficient is this, and the concentration of the species is this. It is also a function of length. That means the longer it passes, the more the decay. The more this is, the ratio actually increases. As a result, the sensitivity of the measurement actually increases.



Now, as we see, many species can have vibrational modes. For example, water is known to be very IR active. The concerned molecule should either have a change in dipole moment, a permanent dipole, or both. So water has a lot of vibrational modes that are IRX. So, if you see this M, which is once again the transition dipole moment, it is given by this expression.

So the permanent dipole can now be expressed in a Taylor series expansion about the internuclear distance Re; this is the expansion where Q is equal to R-Re. μE is the dipole moment when the bond is in equilibrium. And this fluctuating part actually leads to the stretching of the bonds. So, as you can see in these diagrams, there can be asymmetric stretch, symmetric stretch, and bending. So if this is the water molecule, this is H_2O.

Because we are going to show it for the water first. So there can be an asymmetric stretch, which can cause this. There can be a symmetric stretch, and then there can be a bending type of stretch as well. So water has a permanent dipole, and there is a fluctuating dipole moment as well. So the real spectra of water have absorption features

called lines organized into bands associated with particular modes of vibration.

These lines are detected to have very narrow features, but careful observations show that even at those smaller scales, they have definite widths and characteristic shapes. So the line shape functions fall into two general categories; one is homogeneous. This homogeneous line shape occurs when all the molecules in the system have identical line shape functions. It can be inhomogeneous. That means inhomogeneous broadening occurs due to the Maxwell-Boltzmann distribution of molecular velocities.

So the pressure broadening, for example, is known to be homogeneous broadening. Normalized, so pressure broadening leads to what we call a Lorentzian line shape function, and this is given in this particular form. Okay, just know about these things. For a two-level system, the dipole moment oscillates at the broad frequency, except during a collision.

P. Bernard, with one of these references, gives a nice explanation for the collisional broadening. So if the collision is sufficiently strong, the phase of the dipole moment is altered in a random manner by the encounter. So if the average time between the two collisions is t2, then the infinite cosine wave is broken into small pieces of average length t2, as you can see over here. The effect of the collisions will be to convert this infinitely narrow line shape to a line shape that is a function of a finite width. So if we apply the Fourier transform to the broken waveform into frequency components, it results in a Lorentzian line shape with a full width at half maximum given by this particular term.

So this is the pressure broadening that happens. The more the pressure, the more this broadening will be. The Doppler broadening results in an inhomogeneous lineshape. This transition has an intrinsic homogeneous line shape function like this, centered around mu naught prime. The inhomogeneous distribution function, which is called Doppler broadening, is centered around mu naught.

So from Bernard, if the reference stream of the atom is the frequency of the electromagnetic wave, then it is shifted with the atom at rest at the origin of the atomic coordinate system. So it's basically nothing but the Doppler effect. So basically, mu naught is given as 1 plus or minus v by c; c is the velocity of light, v naught prime, the distribution of molecular velocity components for a gas along any given axis, is given by the Maxwell-Boltzmann distribution, which is rather complicated, as you can see. The normalized inhomogeneous Doppler line shape function is therefore given by this expansive expression, and the full width at half maximum is given by this. So the total Doppler line shape, or the line shape, is something like that.

This is actually like a Gaussian function. So if you look closely at the line shapes now, this is the Lorenz profile, which is basically the blue-colored one. We covered it earlier. So this is how it has longer tails and a lower peak. And this is given by this particular expression.

The Doppler profile is given by the red one. which is exactly given by this expression. And the void profile is a convolution of the Doppler and Lorentzian line shapes. The convolution of the two is, therefore, the void line shape function. It is purely homogeneous or purely inhomogeneous in the limiting cases.

For example, at certain pressures, the Lorentzian line shape may actually dominate, giving rise to a predominantly pressure-broadened homogeneous profile, like the one in blue. However, in some cases, for example, where the pressure is extremely low, the Doppler broadening, which is nothing but a velocity effect, might actually dominate. Therefore, the line shape can be given by this well-known Gaussian function. It is more sharply peaked, as we can see, and the Lorentzian has a clear dominance in the far-wing region of the spectrum. Once again, remember that Doppler broadening is basically the shift in frequency.

When it is considered with the atom at rest at the origin of that system. So it is just the same as your Doppler Effect. So this also influences the line shape, the velocity distribution, and it is directly linked to the Maxwell-Boltzmann velocity and the Maxwell-Boltzmann distribution function. So it directly comes from quantum mechanics. So, uh, to do all these things, you know, one might ask the question: where do we get all these numbers, you know, and all these databases which line at which wavelengths the transitions will happen? Because water, being very ion-active, has a lot of species, so HITRAN, which is an acronym for High Resolution Transmission Molecular Absorption Database, is a compilation of spectroscopic parameters.

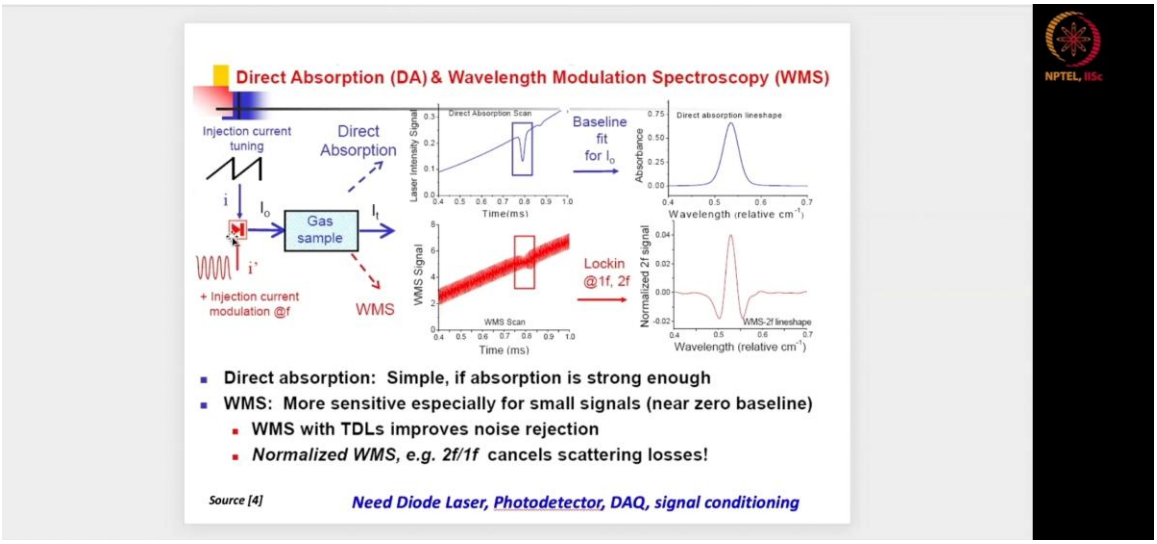
So this database is a long-running project that was started by the Air Force Cambridge Research Laboratory in the 60s, basically to attain knowledge of the infrared properties of the atmosphere, such as high trends in 2000, for example, and there are more recent versions. It contains over 1,080,000 spectral lines for 36 different molecules, not just for water, but water is, of course, an important part; this was originally designed for simulations and analysis of observations in the terrestrial atmosphere. But consequently, the transitions in the bands, which are significant at higher temperatures, may be missing or poorly simulated as a result of that. This is an ongoing effort. So if you look at the transition lines, you will find that they look like something you cannot even isolate.

So this is in the wavelength domain, from 1,300 to 1,500 nanometers, for example. And

this was the light that is, for example, entering this particular sample, which has an absorption concentration c and a path length b; it is entering from this side and exiting through the other side, so this is given by the exponential and path integration, where k is the absorption coefficient and b is the partial pressure, as we know. So this is the absorption coefficient; this is kind of like the number density in the case of water vapor, and this is exactly the partial pressure of water. All right. So the partial pressure can be measured in this way, provided you know the absorption coefficient, which, remember, is a line shape function, and the path length B.

The longer the path length B, the more resolution you get on this measurement. So if you look at this very small portion, the 1306 to 1314 nanometer band, you see that there are countless lines, and these lines do seem to respond with respect to temperature as well. So as the temperature changes, these lines also change. Now they look like straight lines, but if you zoom in, they will have the line-shaped functions, which are given by these.

So they will be broadened. All right. So the proper selection of the wavelength is crucial. And previously, people usually do a high trend simulation for the wavelength selection because then you buy the laser and do all the other stuff. To simulate line shapes at different temperatures and species concentrations, we take water vapor as an example. So this is done at two, actually three, and five different partial pressures and at a constant temperature. This experiment originates in the fuel distribution channels of a PEM fuel cell.



As a result of that, the temperature is more commensurate, but it can also be done for other temperatures. So, these are the temperatures. As you can see, there is a clear-cut

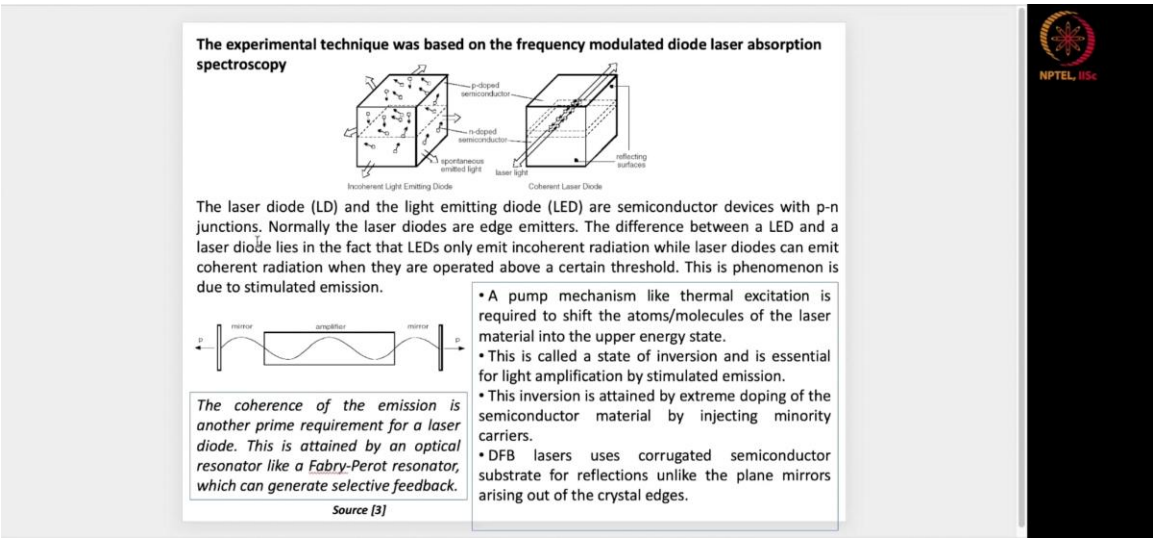
change in the line-shaped patterns. And if you look at the region of interest for this wavelength, this is roughly a nanometer. If it's a nanometer of, well, one centimeter.

So the half width, as we can see, increases with partial pressure, but the maximum intensity decreases with the increase in partial pressure. So, you know, looking at these kinds of curves, if your data shows a sensitivity to partial pressure, which is the concentration, and it also shows a sensitivity to temperature, and the peak also shows a sensitivity, then you have many parameters that you can calibrate. And develop how to measure this particular species or how to measure water vapor concentration with great accuracy. Now, if you do it at different temperatures, for example, you see that the curves are almost overlapping with respect to each other. Here, the partial pressure is held constant; okay, the half-width, of course, does change by a little bit.

Okay, uh. The half-width changes, but the peak, so the variation of half-width with partial pressure is about 38%, while the amplitude variation is a little bit on the lower side. So now we will go to the experimental techniques that we can use for doing this. So, experimental techniques, therefore, if you are going to do it for water, say, for example, we need to use two techniques that are possible. One is direct absorption spectroscopy; another is wavelength modulation spectroscopy. We're not going to cover wavelength modulation in this course.

So what happens is that you need a diode laser, of course, and then this is your gas sample. And so the red color is wavelength modulation, which I urge you to use. The blue one refers to direct absorption. What happens is that you change the current introduced in your diode laser. The change in current actually changes the wavelength.

So you can scan across a particular transition using this current variation. Basically, we do it on a ramp, and we do it very fast. What happens is that the laser intensity, okay, it suddenly shows a tip, okay, because this tip basically corresponds to the absorption. When you do the baseline fit for I naught, you need to have a calibration for the baseline, and there is no absorption. If you divide one by the two and take the log of that, you will get a direct absorption line shape, just like this.



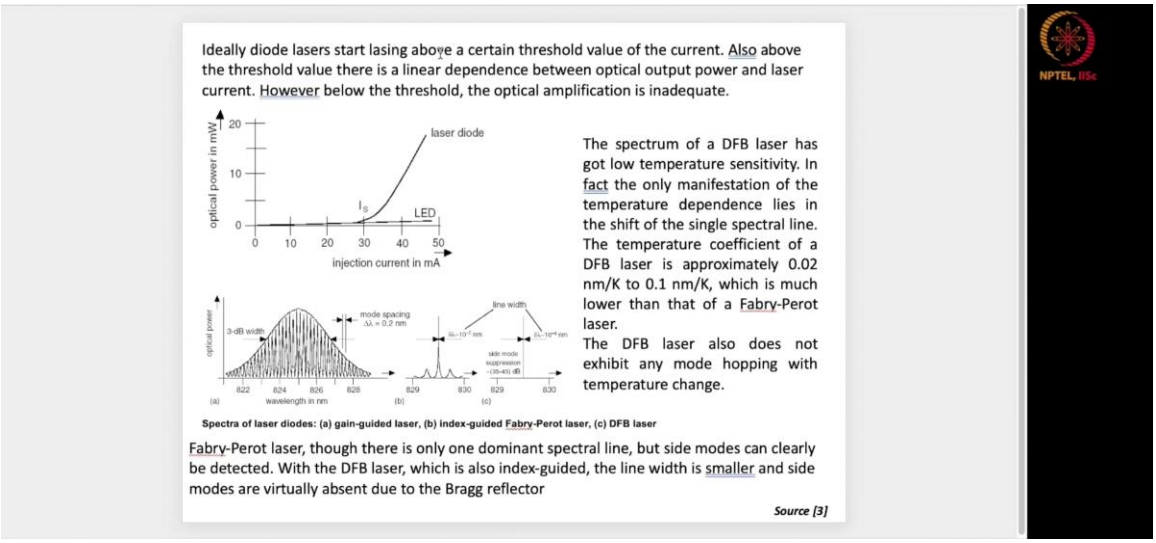
So forget about the wavelength modulation; that is just a technique to give you, you know, more sophistication or sensitivity in the measurement. The direct absorption is simple, but the absorption needs to be strong enough. Of course, for water, it is indeed the case; it is not always the case for other molecules. All right, so in this particular technique, you know, we use a diode laser. The experimental technique was based on frequency-modulated diode laser absorption spectroscopy, and hence it is called the TDLS.

The diode laser and the light-emitting diodes are basically semiconductor devices with PN junctions, so normally the laser diodes are edge emitters. The difference between LEDs and laser diodes lies in the fact that LEDs only emit incoherent radiation, whereas laser diodes can emit coherent radiation when they are operated above a certain threshold. This phenomenon is called stimulated emission. So what happens is that a pump mechanism, like thermal excitation, is required to shift the molecules of the laser into the upper energy state.

This is called the state of inversion. This is common in all lasers, and it is essential for light amplification. This inversion is attained by extreme doping of the semiconductor material with injected minority carriers. The distributed feedback diode lasers use corrugated semiconductors for reflections, unlike plane mirrors. So the coherence of the emission is another prime requirement, and it is attained by something called an optical resonator, like a Fabry-Perot resonator, which can give selective feedback. So these are not crucial, but this is something that is readily available in the market.

So ideally, the diode lasers start lasing above a certain threshold. Value of current. Also,

above the threshold, there is a linear dependence between the optical output power and the laser current. However, below the threshold, optical amplification is inadequate.



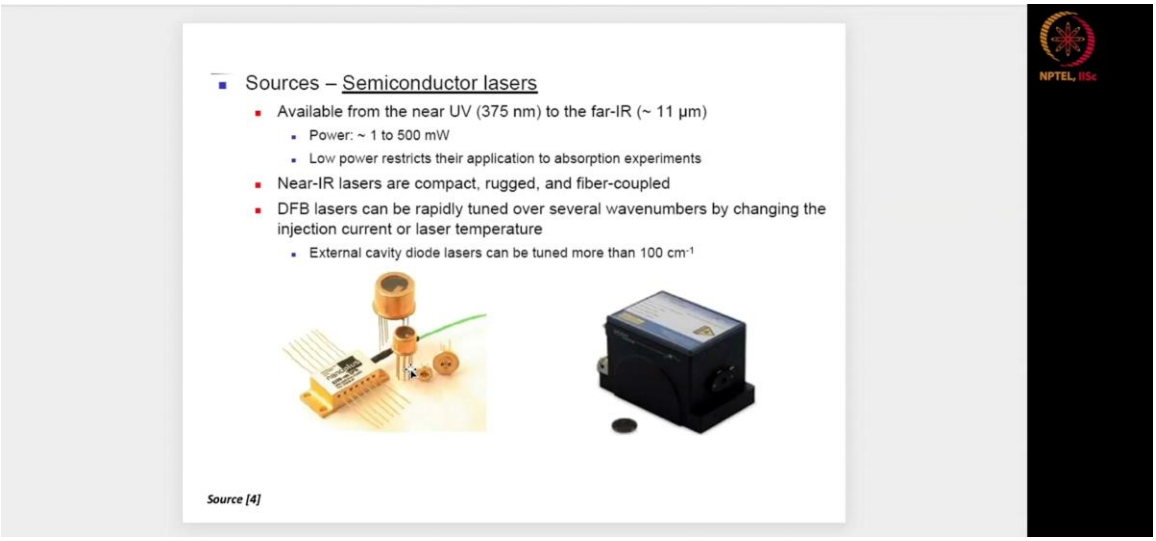
So this is the threshold we are talking about. So beyond a certain injection current only, you can have actually some power. The spectrum of a DFB laser therefore has low temperature sensitivity. In fact, the only manifestation of the temperature dependence lies in the shift of a single spectral line. So, the temperature coefficient of a DFB laser is approximately 0.

02 nanometers per Kelvin. Which is much lower than that of a Fabry-Perot laser. Therefore, it can actually give you the features of the line shape very clearly. And it does not exhibit any mode hopping, meaning it does not shift to any other frequency or any other wavelength with temperature. So in Fabry-Perot lasers, there is only one dominant spectral line. But in DFP lasers, the linewidth is much smaller and the side modes are virtually absent.

So you can basically scan across. It's like a discretization of the entire line shape. And because of this 0.02 nanometers per Kelvin, it can resolve features that are of that order. So these are the semiconductor lasers.

They are available on the market. The near-IR lasers are compact, rugged, and fiber-coupled. The TFV lasers can be rapidly tuned over several wave numbers, except that you have to buy one laser for certain base wavelength. So based on this, you also need photodetectors because you need to measure this I at I_0. A photodiode is a semiconductor

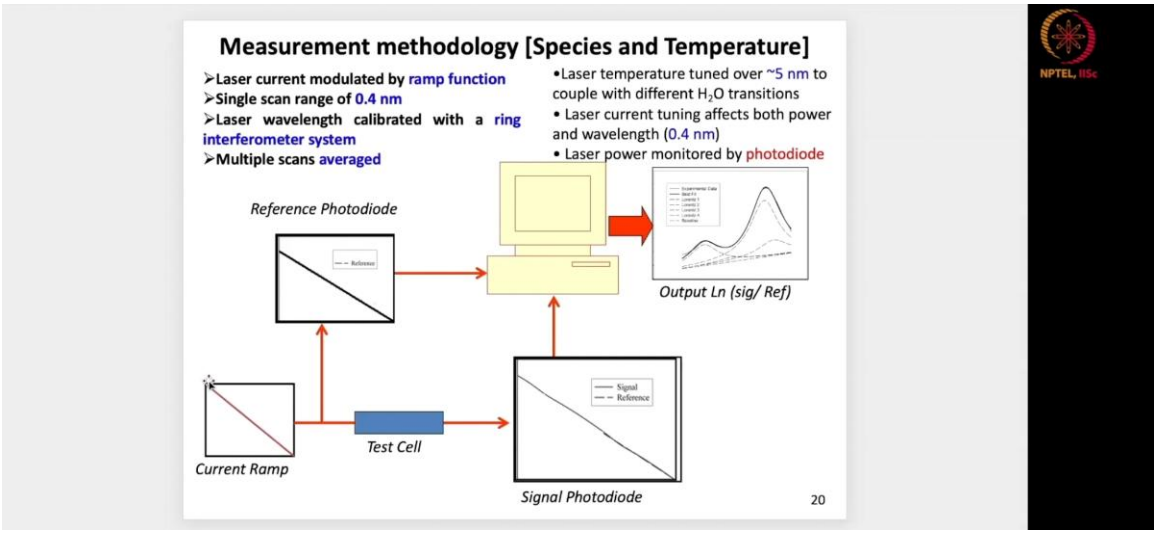
that generates voltage or current when light is incident on it. So, like photoconductors, they have a minimum photon energy associated with them.



before they respond. The source of noise is called Johnson noise. It's not relevant to this particular course. There are many variations of photodiodes, and these are the different detector materials that are routinely used to make the photodiodes. So the measurement methodology is very simple, and the laser is modulated by a RAM function.

And it gives you a scan range of about 0.4 nanometers. Remember, the resolution is 0.02 nanometers per Kelvin. The laser wavelength is calibrated using a ring interferometer. Okay, so this is just to make sure that with the current, we have a definite wavelength associated.

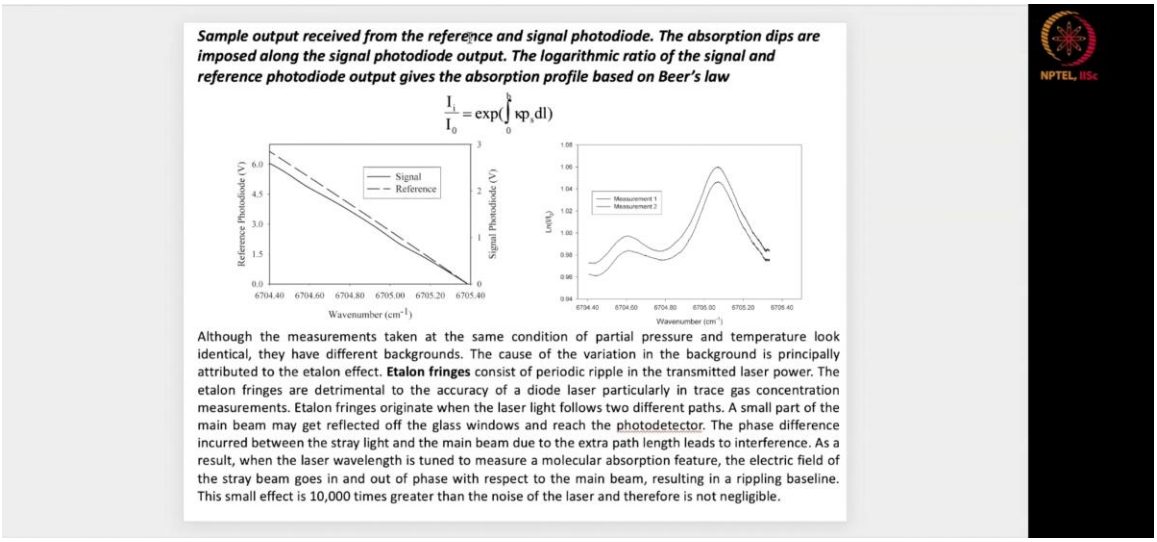
Okay, so that is what has been done. And because you do multiple scans and you do them quickly enough, you get these multiple scans, right? So this is your current ramp. This is your reference. That means it does not undergo absorption.



This has passed through your test cell. This is what you get at the end. So the laser temperature was tuned over 5 nanometers to different H2O transitions. The laser current tuning affects both power and wavelength by about 0.4 nanometers. The laser power is monitored by a photodiode. So the absorption of monochromatic light, if you look at it, is like the scan wavelength.

This is a line-of-sight-based measurement. That means you need a thorough and complete passage. So this is given by the Beer-Lambert relationships, which we already covered. And this is the spectral absorption coefficient, which is basically what the light shape function is all about. And that is what actually responds to the changes, as well. So the sample received from the photodiode and the reference signal, the absorption dips are imposed on the photodiode output signal given here.

Although the measurements are taken under the same conditions of partial pressure and temperature, and they look identical, they have different backgrounds. The cause of this variation in background is principally associated with etaloning because there is a slight shift in the background. The etalon fringes consist of periodic ripples in the transmitted laser power. These are detrimental to the accuracy of detectors, so you have to take care of them. But you can also switch and you can do whatever mathematical mathematical transitions on this without disturbing the relative tip that is there in the signal.



So the effect is higher; usually, the data loading effect is higher than the noise and therefore negligible. You need to take care of that. So you skip the wavelength modulation part because it is not important. So the absorption-based sensors have the highest sensitivity and selectivity. When you are probing a spectrally narrow feature, the tuning of the source across the absorption features distinguishes the isolated feature from the background absorption, scattering, extinction, or whatever is there.

It is very sensitive. And it's relevant to gas dynamics and combustion flows, as well as for exclusive detections; you know, anything that absorbs radiation. With the exception of visible transitions of O2 and NO2, the absorption measurements are performed on overtones and combinations of vibrations. The typical line strengths of the transitions are as follows. 10 to the power of minus 23 to 10 to the power of minus 21, which is two to three orders of magnitude below the fundamental vibrational rate of TdIr.

So these are some of the more detailed aspects of absorption spectroscopy. These other small species also have discrete rotational transitions; larger molecules and hydrocarbon fuels also have the same. So technically, you can measure a lot, and you can even multiplex across multiple wavelengths. All it needs is for you to have different diode lasers. You combine them through a fiber coupler and pass one of them through a reference. And the other one, you pass through the gas, and therefore you can probe multiple wavelengths and scan across multiple wavelengths for multi-species measurements.

Overview of near-IR and visible spectroscopy of gas-dynamic and combustion species

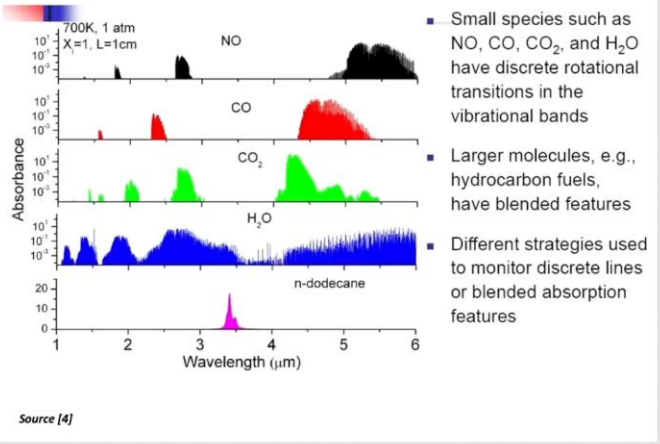
- Absorption-based sensors have the highest sensitivity and selectivity when a spectrally narrow source is used to probe a spectrally narrow feature.
- Tuning the wavelength of the source across the absorption feature distinguishes the isolated feature from background absorption, scattering, or extinction effects due to obscuration of the optical path or changes in the total source power coupled onto the receiver
- Thus, most applications relevant to gas-dynamic and combustion flows are based on absorption by low molecular- weight molecules with well resolved absorption transitions

- With the exception of visible transitions of O2 and NO2, the absorption measurements are performed on overtone and combination vibrational absorption bands.
- Typical linestrengths of these transitions are between 10^{-23} and 10^{-21} cm/*molecule, two to three orders of magnitude* below the fundamental vibrational transitions in the mid-IR

- A number of molecules of interest in combustion flows possess transitions near the important 1.*55 microns spectral* window.
- Carbon monoxide has a second overtone band centred at 1.*575 microns (Cassidy and Bonnell 1988, Hanson* 1997, Sonnenfroh and Allen 1997a, Mihalcea *et al 1997,* Gabrysch M *et al 1997).*
- The OH radical's first overtone band extends throughout this region with linestrengths at typical flame conditions of $5x10^{-21}$ cm/*molecule and is easily* detected in laboratory flames (Sonnenfroh and Allen 1996a, Upschulte *et al 1998)*
- Second overtone transitions of NO near 1:*8 m have recently been identified and* detected in ambient and combustion gases using a DFB laser (Sonnenfroh and Allen 1997b)

Source [5]

Okay, so this is, for example, the absorbance of CH4, CO2, and water, which is obviously the largest. You see that you can use different lasers to probe different species. So this is rather good, and this can be used basically to probe and get all the species at the same time. So we know why the species can be detected because the concentration is directly related to the ratio of the intensities.

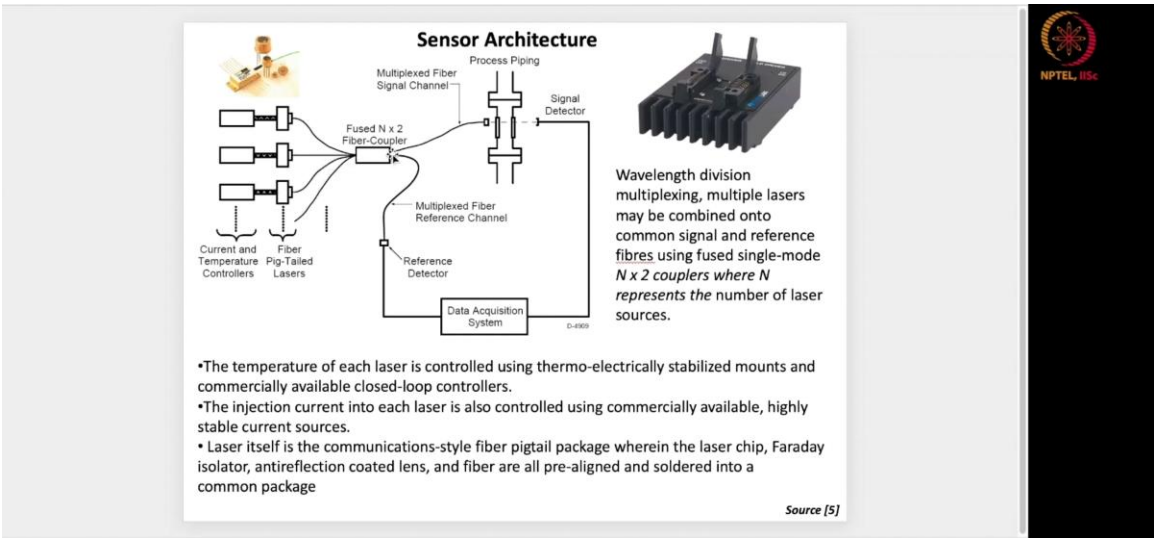


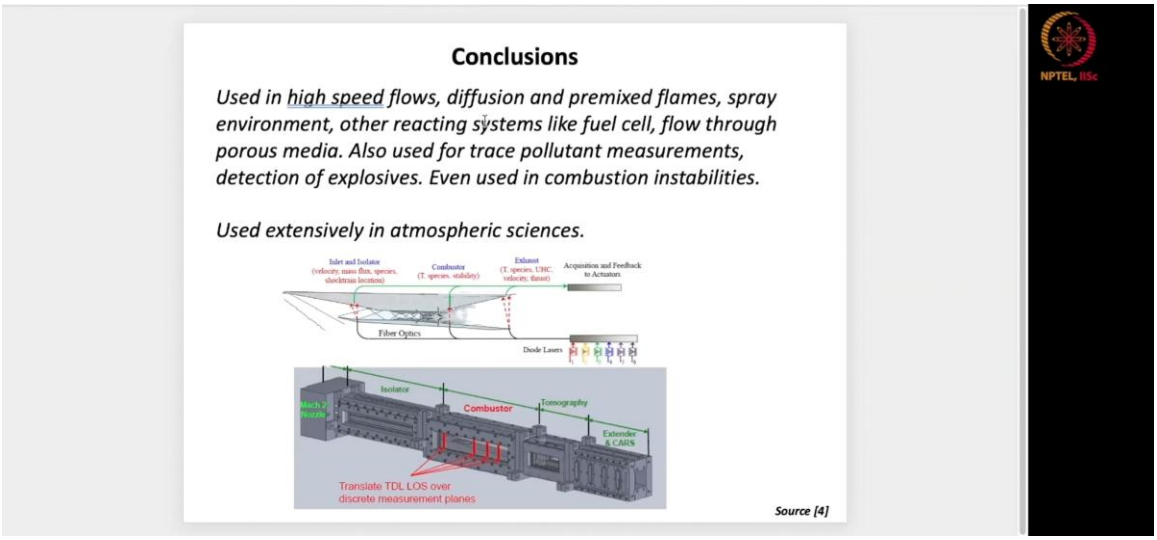
- Small species such as NO, CO, CO_2, and H_2O have discrete rotational transitions in the vibrational bands
- Larger molecules, e.g., hydrocarbon fuels, have blended features
- Different strategies used to monitor discrete lines or blended absorption features

Source [4]

And we showed why that is the case. And this can also be done for Gino and other types of species. So it is also used for high-speed flows, diffusion, premixed flows, spray environments, other reacting systems like fuel cells, flow through porous media, trace pollutant measurements, detection of explosives, and even combustion instabilities. And

it is extensively used in atmospheric science. As we saw, HYPETREN was a database that actually included atmospheric sciences. So these are the references that we wrote: source one, source two, source three, as you can see.





So Bernard has written a very good book on the spectra of atoms and molecules. And you can see Ron Hansen's lecture on tunable diode laser-based absorption spectroscopy, M.G. Allen's Measurement Science and Technology paper. Mark Holden's lectures on molecular spectroscopy at Princeton Summer School. And of course, there are other references as well, as we can see; but these are the references that are useful.

So, to cut a very long story short, if I have to say it in a few words, we can readily see that absorption spectroscopy is a very versatile tool. Ultimately, it comes down to very

simple forms that, if you know the absorption cross-section and if you know I over I0, you can technically find out what the concentration will be. Now, to find out this absorption line shape, you need to do a little bit of quantum mechanics; at the same time, you also need to know what the sources of broadening are. Quantum mechanics will explain how radiation interacts with matter; then, of course, you will observe the broadening effects due to the simple reason of detuning, the non-radiative decay due to collisions, and due to droplets. Thus, there is homogeneous line broadening and inhomogeneous broadening, all of which are very well understood.

So, if you put all of them into the picture, you will be in a position to measure any type of species. Now, you can multiply; you need a diode laser, of course, for this business because they can scan across very. Narrow bands. They have very high resolutions, so when you change the current, you change the wavelength; that's how you scan a band.

But it is on a ramp, so the power also changes; therefore, you need a reference. Everything actually goes up on a ramp, so if you divide one by the other, you get the ratio, and that can be used for measuring explosives and whatever you want. It can be used in high-speed flows, low-speed flows, trace pollution measurements, and detection of explosives. Thank you.