Statistical Thermodynamics for Engineers
Professor Saptarshi Basu
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Lecture 59
Theory of Absorption Spectroscopy

So, welcome to lecture number 48 of the Statistical Thermodynamics course for engineers. So, during the last lecture, if you recall, we calculated the oscillating dipole movement, which is given by this.

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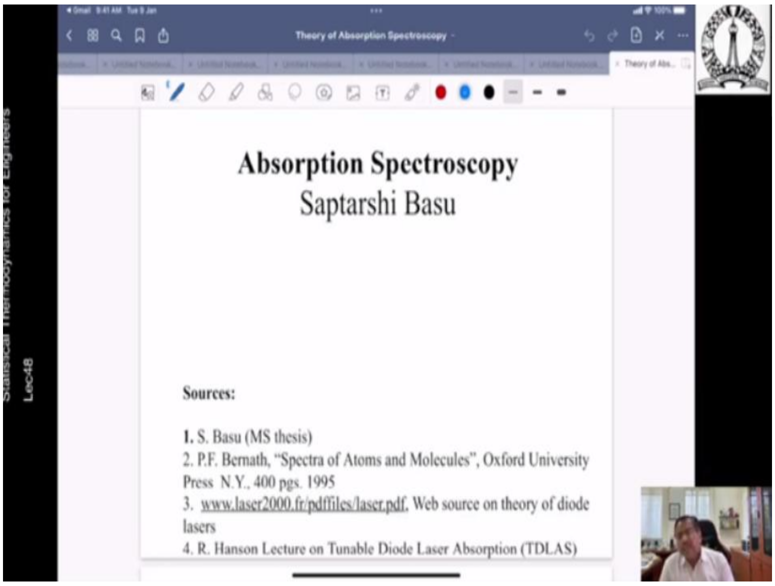

Absorption Spectroscopy

Saptarshi Basu

Sources:

1. S. Basu (MS thesis)
2. P.F. Bernath, "Spectra of Atoms and Molecules", Oxford University Press N.Y., 400 pgs. 1995
3. www.laser2000.fr/pdffiles/laser.pdf, Web source on theory of diode lasers
4. R. Hanson Lecture on Tunable Diode Laser Absorption (TDLAS)

Now, that we have got an idea that, what absorptions, we can now set the stage for the absorptions spectroscopy. So, we are going to do a little bit of rehash of what we already did in this PPT. So, the sources are basically Bernath, which is "Spectra of Atoms and Molecules". The MS thesis of Professor S Basu. And then there are wave lecturers and Hansen is, professor Ronald Hansen is lecture on Tunable Diode Laser Spectroscopy.

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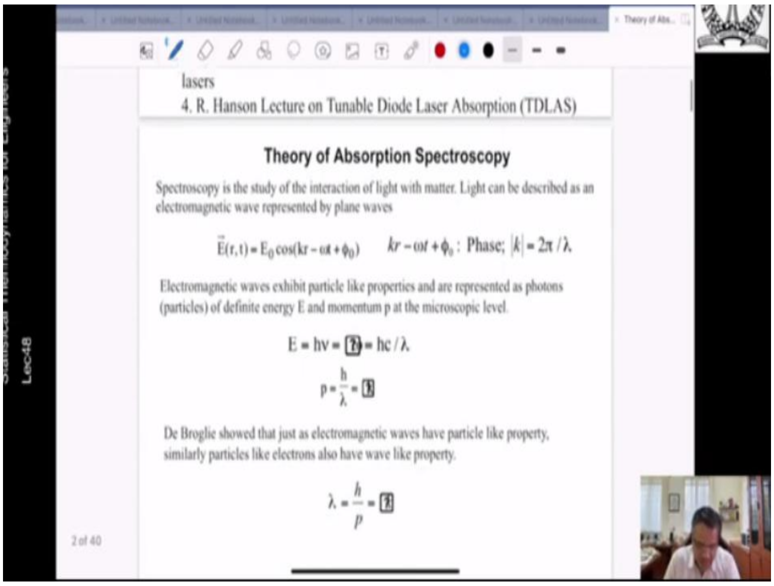


lasers

4. R. Hanson Lecture on Tunable Diode Laser Absorption (TDLAS)

Theory of Absorption Spectroscopy

Spectroscopy is the study of the interaction of light with matter. Light can be described as an electromagnetic wave represented by plane waves

$$\vec{E}(r,t) = E_0\cos(kr - \omega t + \phi_0) \qquad kr - \omega t + \phi_0 :\ \text{Phase};\ |k| = 2\pi/\lambda$$

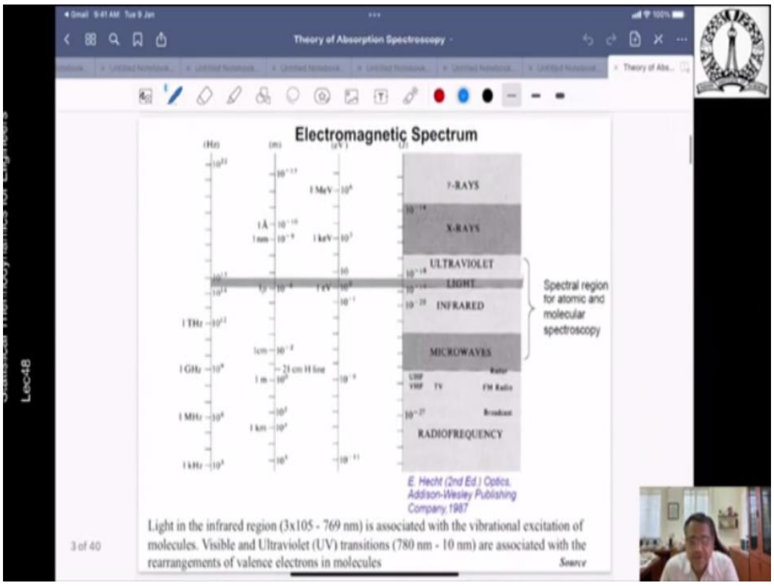
Electromagnetic waves exhibit particle like properties and are represented as photons (particles) of definite energy E and momentum p at the microscopic level.

$$E = h\nu = \boxed{?} = hc/\lambda$$

$$p = \frac{h}{\lambda} = \boxed{?}$$

De Broglie showed that just as electromagnetic waves have particle like property, similarly particles like electrons also have wave like property.

$$\lambda = \frac{h}{p} = \boxed{?}$$

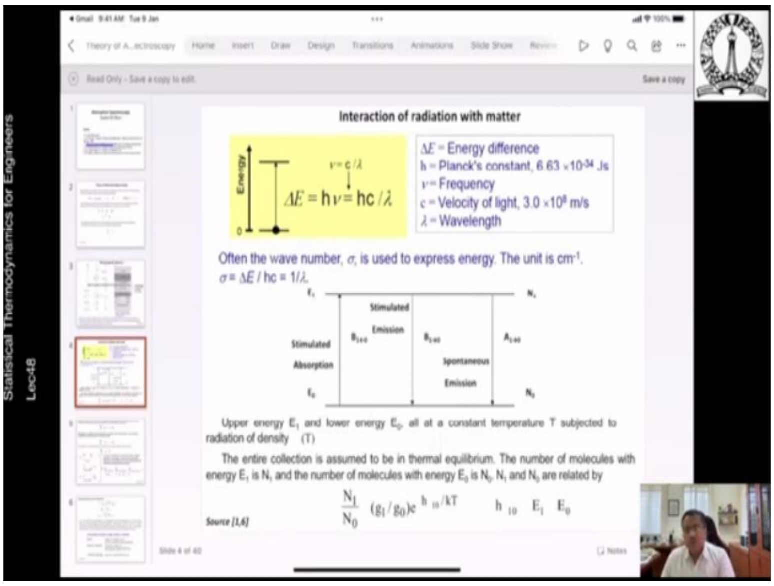


Electromagnetic Spectrum

E. Hecht (2nd Ed.) Optics, Addison-Wesley Publishing Company 1987

Light in the infrared region (3x105 - 769 nm) is associated with the vibrational excitation of molecules. Visible and Ultraviolet (UV) transitions (780 nm - 10 nm) are associated with the rearrangements of valence electrons in molecules

Source



Interaction of radiation with matter

$$\Delta E = h\nu = hc/\lambda$$

ΔE = Energy difference
h = Planck's constant, 6.63×10^{-34} Js
ν = Frequency
c = Velocity of light, 3.0×10^{8} m/s
λ = Wavelength

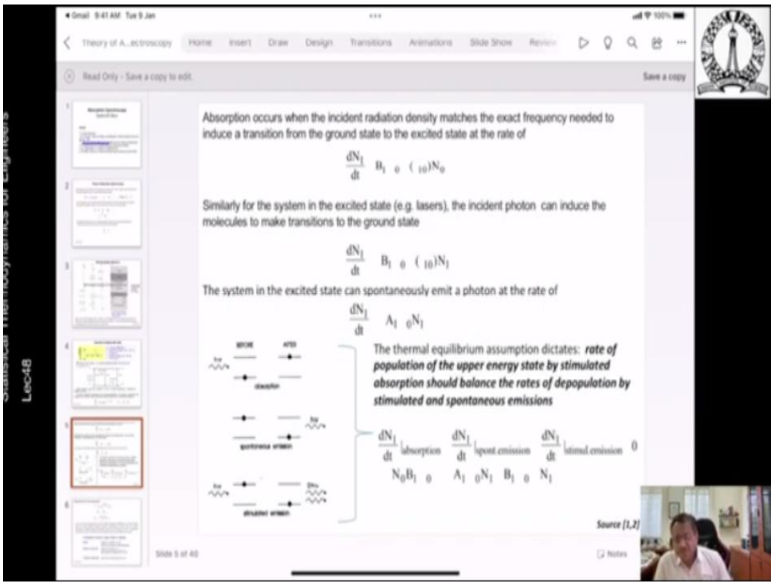
Often the wave number, σ, is used to express energy. The unit is cm^{-1}.
$\sigma = \Delta E / hc = 1/\lambda$

Upper energy E_1 and lower energy E_0, all at a constant temperature T subjected to radiation of density (T)

The entire collection is assumed to be in thermal equilibrium. The number of molecules with energy E_1 is N_1 and the number of molecules with energy E_0 is N_0. N_1 and N_0 are related by

$$\frac{N_1}{N_0} \quad (g_1/g_0)e^{h\,_{10}/kT} \qquad h\,_{10} \quad E_1 \quad E_0$$

Source [1,6]



Absorption occurs when the incident radiation density matches the exact frequency needed to induce a transition from the ground state to the excited state at the rate of

$$\frac{dN_1}{dt} \quad B_{1\ 0} \ (\ _{10})N_0$$

Similarly for the system in the excited state (e.g. lasers), the incident photon can induce the molecules to make transitions to the ground state

$$\frac{dN_1}{dt} \quad B_{1\ 0} \ (\ _{10})N_1$$

The system in the excited state can spontaneously emit a photon at the rate of

$$\frac{dN_1}{dt} \quad A_{1\ 0}N_1$$

The thermal equilibrium assumption dictates: ***rate of population of the upper energy state by stimulated absorption should balance the rates of depopulation by stimulated and spontaneous emissions***

$$\frac{dN_1}{dt}\Big|_{absorption} \quad \frac{dN_1}{dt}\Big|_{spont\ emission} \quad \frac{dN_1}{dt}\Big|_{stimul\ emission} \quad 0$$

$$N_0B_{1\ 0} \quad A_{1\ 0}N_1 \quad B_{1\ 0} \quad N_1$$

Source [1,2]

So, some of these things we already did, if you recall. So, there is no point in doing this. We know the electromagnetic spectrum already by heart right now, and we also have done the interaction of radiation with matter, which essentially translates to the interaction of radiation with matter. That means what is the energy difference and stuff like that.

So, we are already aware of things like, we have already done this earlier that how interaction of radiation happens with matter by the two-level diagram that you see over here that, E1 and E naught. So, these parts are quite clear. And then we also did that when radiation, absorption of radiation occurs, the incident radiation, density matches the exact frequency, and then we have calculated the different rate constants based on that. So, as you can see therefore, so, so these were the different rate constants. These were the different rates of population of the upper state in the lower state.

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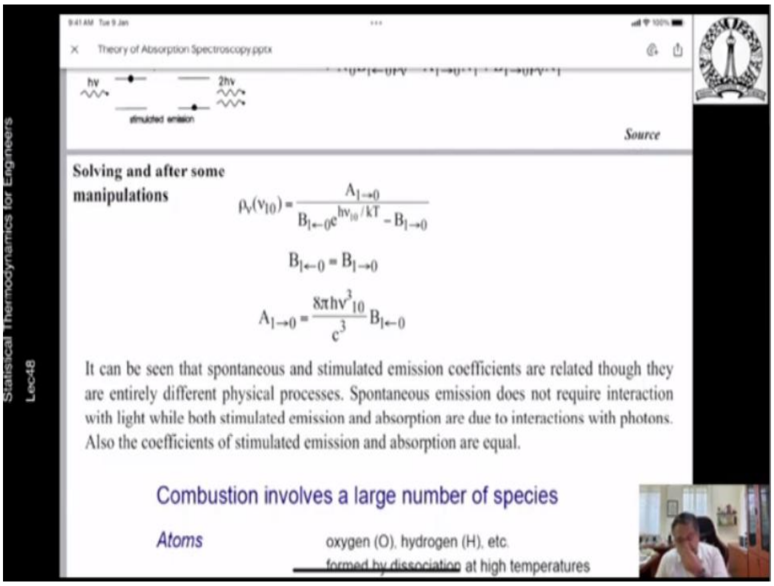


Source

Solving and after some manipulations

$$\rho_v(v_{10}) = \frac{A_{1\to 0}}{B_{1\leftarrow 0}e^{hv_{10}/kT} - B_{1\to 0}}$$

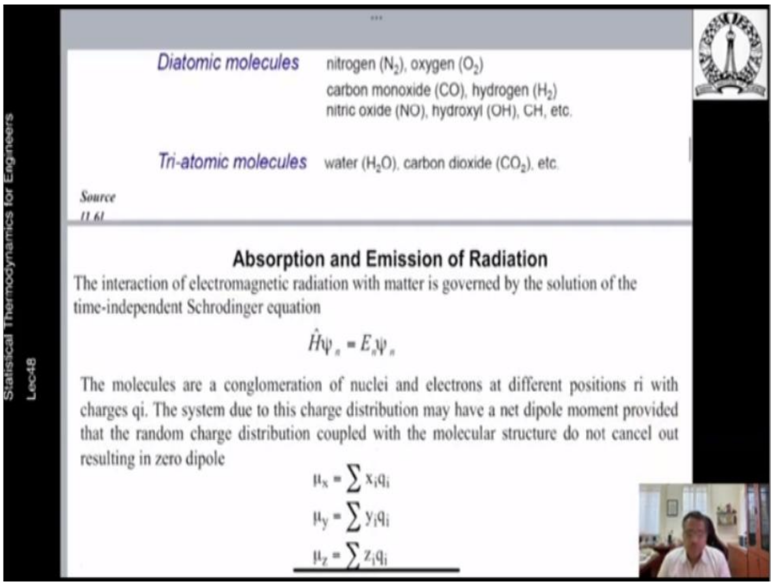
$$B_{1\leftarrow 0} = B_{1\to 0}$$

$$A_{1\to 0} = \frac{8\pi h v^3_{10}}{c^3} B_{1\leftarrow 0}$$

It can be seen that spontaneous and stimulated emission coefficients are related though they are entirely different physical processes. Spontaneous emission does not require interaction with light while both stimulated emission and absorption are due to interactions with photons. Also the coefficients of stimulated emission and absorption are equal.

Combustion involves a large number of species

Atoms	oxygen (O), hydrogen (H), etc. formed by dissociation at high temperatures



Diatomic molecules	nitrogen (N_2), oxygen (O_2) carbon monoxide (CO), hydrogen (H_2) nitric oxide (NO), hydroxyl (OH), CH, etc.
Tri-atomic molecules	water (H_2O), carbon dioxide (CO_2), etc.

Source
[1,6]

Absorption and Emission of Radiation

The interaction of electromagnetic radiation with matter is governed by the solution of the time-independent Schrodinger equation

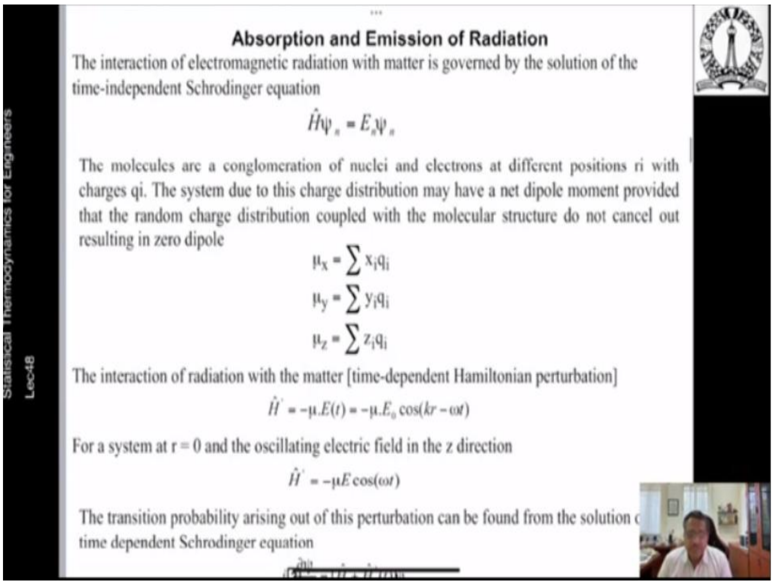
$$\hat{H}\psi_n = E_n\psi_n$$

The molecules are a conglomeration of nuclei and electrons at different positions ri with charges qi. The system due to this charge distribution may have a net dipole moment provided that the random charge distribution coupled with the molecular structure do not cancel out resulting in zero dipole

$$\mu_x = \sum x_i q_i$$

$$\mu_y = \sum y_i q_i$$

$$\mu_z = \sum z_i q_i$$



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$$\mu_x = \sum x_i q_i$$

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$$\mu_z = \sum z_i q_i$$

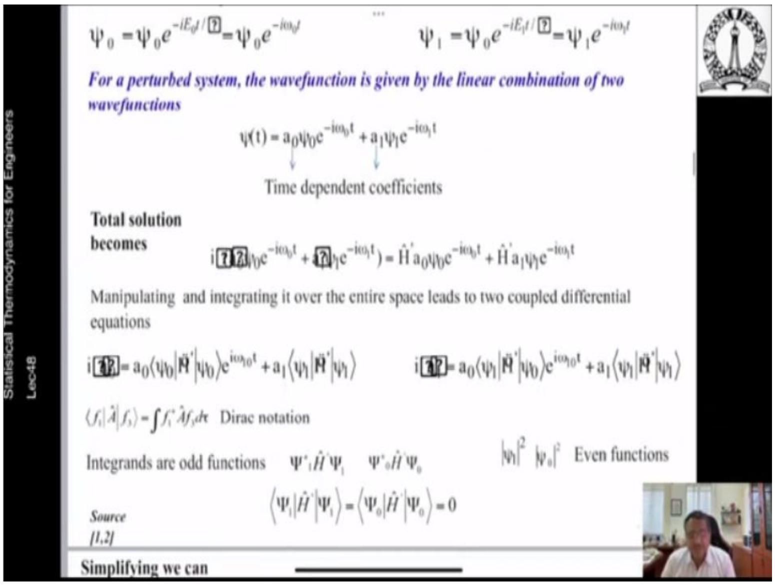
The interaction of radiation with the matter [time-dependent Hamiltonian perturbation]

$$\hat{H}' = -\mu.E(t) = -\mu.E_0 \cos(kr - \omega t)$$

For a system at r = 0 and the oscillating electric field in the z direction

$$\hat{H}' = -\mu E \cos(\omega t)$$

The transition probability arising out of this perturbation can be found from the solution
time dependent Schrodinger equation



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$\psi_0 = \psi_0 e^{-iE_0 t/\boxed{?}} = \psi_0 e^{-i\omega_0 t}$ $\psi_1 = \psi_0 e^{-iE_1 t/\boxed{?}} = \psi_1 e^{-i\omega_1 t}$

For a perturbed system, the wavefunction is given by the linear combination of two wavefunctions

$$\psi(t) = a_0\psi_0 e^{-i\omega_0 t} + a_1\psi_1 e^{-i\omega_1 t}$$

Time dependent coefficients

Total solution becomes

$$i\boxed{?}\boxed{?}\psi_0 e^{-i\omega_0 t} + \boxed{?}\psi_1 e^{-i\omega_1 t}) = \hat{H}' a_0\psi_0 e^{-i\omega_0 t} + \hat{H}' a_1\psi_1 e^{-i\omega_1 t}$$

Manipulating and integrating it over the entire space leads to two coupled differential equations

$$i\boxed{?} = a_0\langle\psi_0|\hat{H}'|\psi_0\rangle e^{i\omega_{10}t} + a_1\langle\psi_1|\hat{H}'|\psi_1\rangle \qquad i\boxed{?} = a_0\langle\psi_1|\hat{H}'|\psi_0\rangle e^{i\omega_{10}t} + a_1\langle\psi_1|\hat{H}'|\psi_1\rangle$$

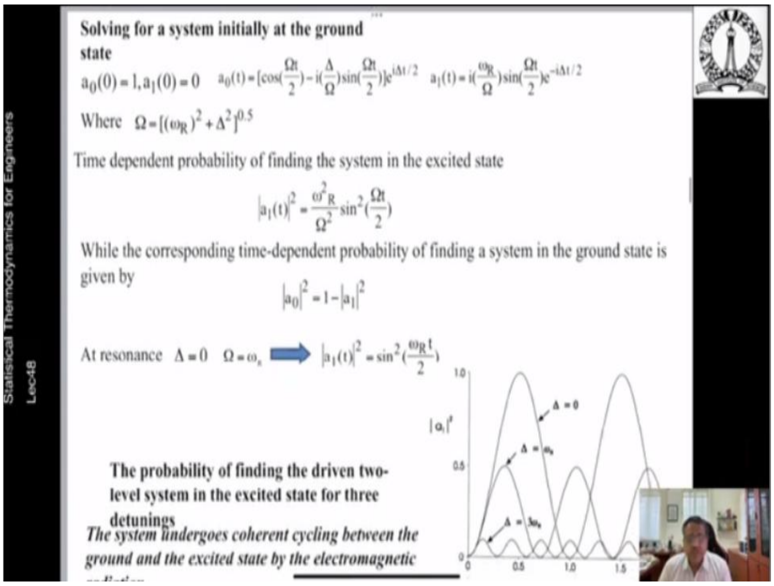
$\langle f_i|\hat{A}|f_j\rangle = \int f_i^* \hat{A} f_j d\tau$ Dirac notation

Integrands are odd functions $\Psi^*_1 \hat{H}' \Psi_1$ $\Psi^*_0 \hat{H}' \Psi_0$ $|\psi_1|^2$ $|\psi_0|^2$ Even functions

$$\langle\Psi_1|\hat{H}'|\Psi_1\rangle = \langle\Psi_0|\hat{H}'|\Psi_0\rangle = 0$$

Source [1,2]

Simplifying we can



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Solving for a system initially at the ground state

$a_0(0) = 1, a_1(0) = 0$ $a_0(t) = [\cos(\frac{\Omega t}{2}) - i(\frac{\Delta}{\Omega})\sin(\frac{\Omega t}{2})]e^{i\Delta t/2}$ $a_1(t) = i(\frac{\omega_R}{\Omega})\sin(\frac{\Omega t}{2})e^{-i\Delta t/2}$

Where $\Omega = [(\omega_R)^2 + \Delta^2]^{0.5}$

Time dependent probability of finding the system in the excited state

$$|a_1(t)|^2 = \frac{\omega^2_R}{\Omega^2}\sin^2(\frac{\Omega t}{2})$$

While the corresponding time-dependent probability of finding a system in the ground state is given by

$$|a_0|^2 = 1 - |a_1|^2$$

At resonance $\Delta = 0$ $\Omega = \omega_R$ $\Rightarrow$ $|a_1(t)|^2 = \sin^2(\frac{\omega_R t}{2})$

The probability of finding the driven two-level system in the excited state for three detunings

The system undergoes coherent cycling between the ground and the excited state by the electromagnetic

And this is how we calculated, if you recall, the, how the spontaneous and the stimulated emission coefficient are evaluated. So, for example, in an application like combustion, you have a lot of species, oxygen, nitrogen, nitrogen, oxygen, water vapor, and CO2. So, absorption and emission of radiation then we said is given by the time independent Schrodinger wave equation. And then we solved for the dipole moment, and then we calculated the time dependent coefficients. Forgive me about the symbols over here. So, these are all covered in the previous classes.

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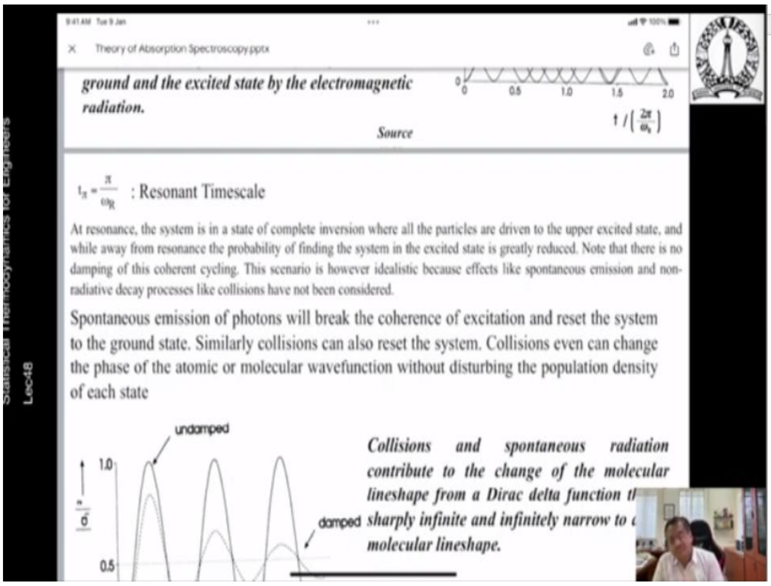

Theory of Absorption Spectroscopy.pptx

ground and the excited state by the electromagnetic radiation.

Source

$t_\pi = \frac{\pi}{\omega_R}$: Resonant Timescale

At resonance, the system is in a state of complete inversion where all the particles are driven to the upper excited state, and while away from resonance the probability of finding the system in the excited state is greatly reduced. Note that there is no damping of this coherent cycling. This scenario is however idealistic because effects like spontaneous emission and non-radiative decay processes like collisions have not been considered.

Spontaneous emission of photons will break the coherence of excitation and reset the system to the ground state. Similarly collisions can also reset the system. Collisions even can change the phase of the atomic or molecular wavefunction without disturbing the population density of each state

Collisions and spontaneous radiation contribute to the change of the molecular lineshape from a Dirac delta function th sharply infinite and infinitely narrow to a molecular lineshape.

So, we also know that what are the de detailing frequencies, and the resonant time scales. So, spontaneous emission of photons, for example, we said will break the coherence of excitation and reset the system to the ground state. Similarly, collisions can also reset the system, so collisions even can change the face of the atomic or molecule wave function without disturbing the population density of each of the states.

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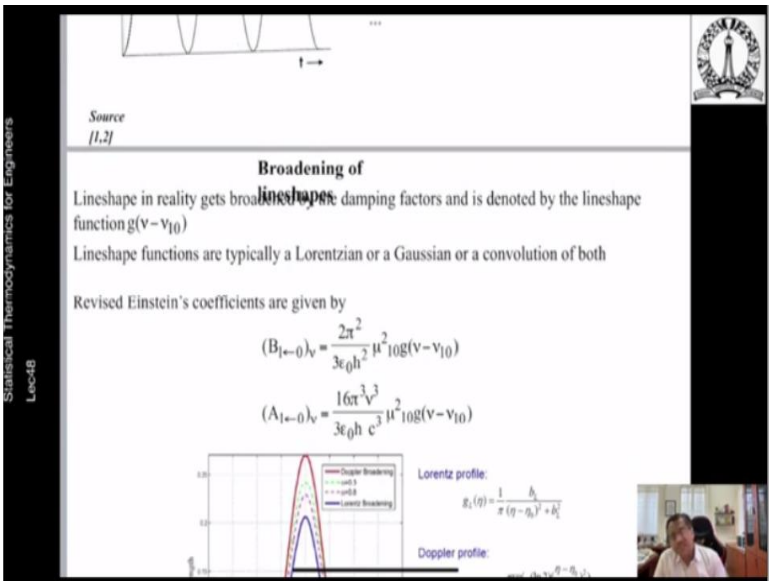


Source [1,2]

Broadening of lineshapes

Lineshape in reality gets broadened by the damping factors and is denoted by the lineshape function $g(\nu - \nu_{10})$

Lineshape functions are typically a Lorentzian or a Gaussian or a convolution of both

Revised Einstein's coefficients are given by

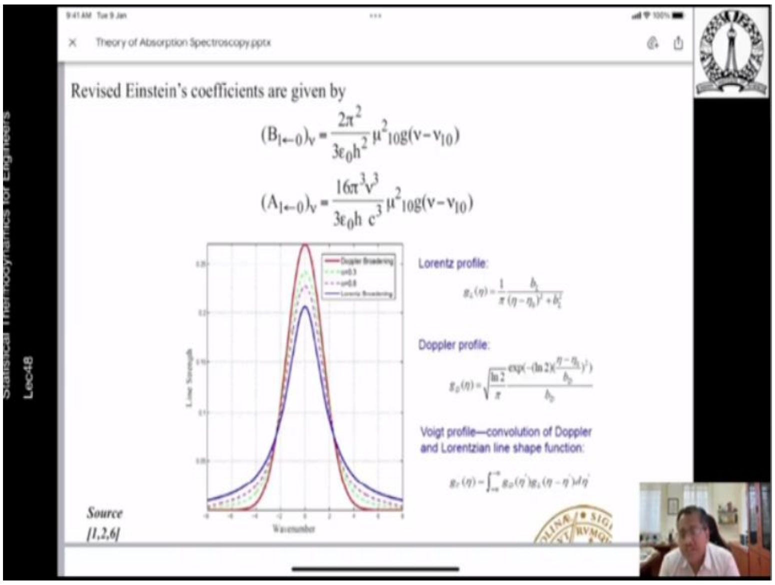
$$(B_{1\leftarrow 0})_\nu = \frac{2\pi^2}{3\varepsilon_0 h^2}\mu^2_{10} g(\nu - \nu_{10})$$

$$(A_{1\leftarrow 0})_\nu = \frac{16\pi^3\nu^3}{3\varepsilon_0 h c^3}\mu^2_{10} g(\nu - \nu_{10})$$

Lorentz profile:

$$g_L(\eta) = \frac{1}{\pi}\frac{b_L}{(\eta - \eta_0)^2 + b_L^2}$$

Doppler profile:



Revised Einstein's coefficients are given by

$$(B_{1\leftarrow 0})_v = \frac{2\pi^2}{3\varepsilon_0 h^2}\mu^2_{10}g(v-v_{10})$$

$$(A_{1\leftarrow 0})_v = \frac{16\pi^3 v^3}{3\varepsilon_0 h\, c^3}\mu^2_{10}g(v-v_{10})$$

Lorentz profile:

$$g_L(\eta) = \frac{1}{\pi}\frac{b_L}{(\eta-\eta_0)^2+b_L^2}$$

Doppler profile:

$$g_D(\eta) = \sqrt{\frac{\ln 2}{\pi}}\frac{\exp(-(\ln 2)(\frac{\eta-\eta_0}{b_D})^2)}{b_D}$$

Voigt profile—convolution of Doppler and Lorentzian line shape function:

$$g_V(\eta) = \int_{-\infty}^{\infty} g_D(\eta')g_L(\eta-\eta')d\eta'$$

Source [1,2,6]

We also saw that the line shape in reality gets broadened by the damping factors, and it is given by the line shape function, which we saw. So, for example, if you look at this slot over here, this shows the Lorentzian blood broadening and the doppler broadening. So, the Lorentzian profile is given by that equation, which you see the Lorenz profile, and then there is something called doppler broadening, which happens because of the motion of the molecules. Lorenz profile comes from the pressure broadening. So, together the convolution of the doppler and the Lorentzian line shape function gives you the, the final line shape, which is for the Voigt profile.

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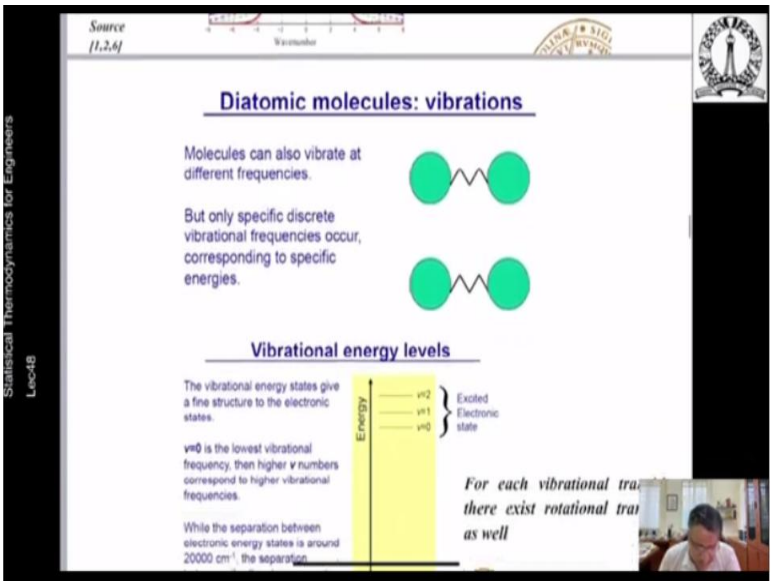


Source [1,2,6]

Diatomic molecules: vibrations

Molecules can also vibrate at different frequencies.

But only specific discrete vibrational frequencies occur, corresponding to specific energies.

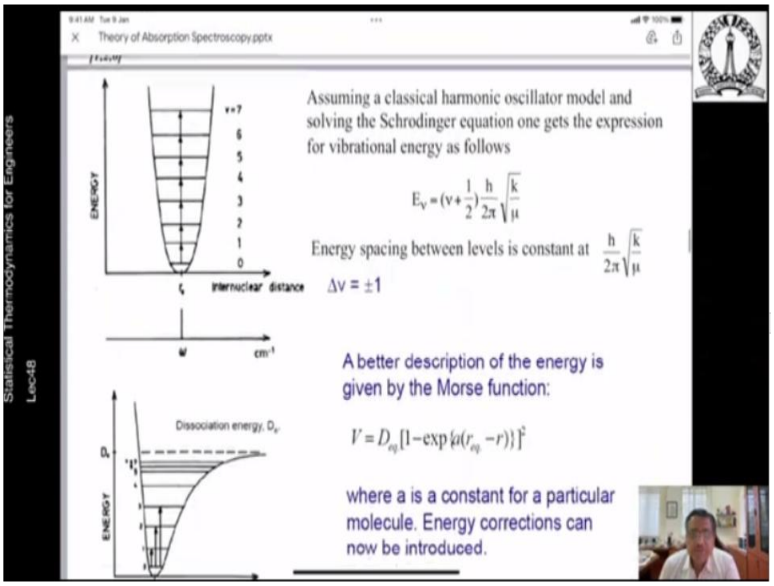
Vibrational energy levels

The vibrational energy states give a fine structure to the electronic states.

v=0 is the lowest vibrational frequency, then higher ***v*** numbers correspond to higher vibrational frequencies.

While the separation between electronic energy states is around 20000 cm^{-1}, the separation

For each vibrational tra
there exist rotational tra
as well



Assuming a classical harmonic oscillator model and solving the Schrodinger equation one gets the expression for vibrational energy as follows

$$E_v = (v+\frac{1}{2})\frac{h}{2\pi}\sqrt{\frac{k}{\mu}}$$

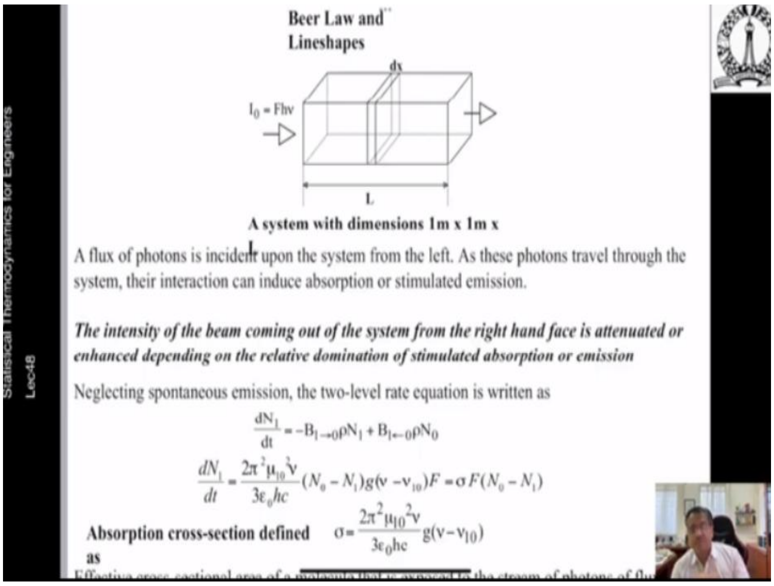
Energy spacing between levels is constant at $\frac{h}{2\pi}\sqrt{\frac{k}{\mu}}$

$\Delta v = \pm 1$

A better description of the energy is given by the Morse function:

$$V = D_{eq}[1-\exp\{a(r_{eq}-r)\}]^2$$

where a is a constant for a particular molecule. Energy corrections can now be introduced.



Beer Law and Lineshapes

A system with dimensions 1m x 1m x

A flux of photons is incident upon the system from the left. As these photons travel through the system, their interaction can induce absorption or stimulated emission.

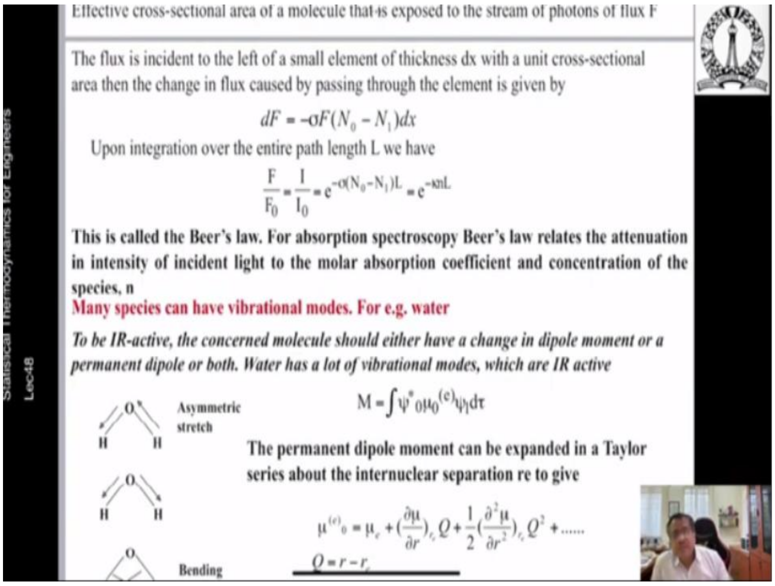
The intensity of the beam coming out of the system from the right hand face is attenuated or enhanced depending on the relative domination of stimulated absorption or emission

Neglecting spontaneous emission, the two-level rate equation is written as

$$\frac{dN_1}{dt} = -B_{1\to 0}\rho N_1 + B_{1\leftarrow 0}\rho N_0$$

$$\frac{dN_1}{dt} = \frac{2\pi^2\mu_{10}^2\nu}{3\varepsilon_0 hc}(N_0 - N_1)g(\nu-\nu_{10})F = \sigma F(N_0 - N_1)$$

Absorption cross-section defined as $\sigma = \frac{2\pi^2\mu_{10}^2\nu}{3\varepsilon_0 hc}g(\nu-\nu_{10})$



Effective cross-sectional area of a molecule that is exposed to the stream of photons of flux F

The flux is incident to the left of a small element of thickness dx with a unit cross-sectional area then the change in flux caused by passing through the element is given by

$$dF = -\sigma F(N_0 - N_1)dx$$

Upon integration over the entire path length L we have

$$\frac{F}{F_0} = \frac{I}{I_0} = e^{-\sigma(N_0-N_1)L} = e^{-\kappa nL}$$

This is called the Beer's law. For absorption spectroscopy Beer's law relates the attenuation in intensity of incident light to the molar absorption coefficient and concentration of the species, n

Many species can have vibrational modes. For e.g. water

To be IR-active, the concerned molecule should either have a change in dipole moment or a permanent dipole or both. Water has a lot of vibrational modes, which are IR active

Asymmetric stretch

$$M = \int \psi^*{}_0\mu_0{}^{(e)}\psi_1 d\tau$$

The permanent dipole moment can be expanded in a Taylor series about the internuclear separation re to give

$$\mu^{(e)}{}_0 = \mu_e + (\frac{\partial\mu}{\partial r})_{r_e}Q + \frac{1}{2}(\frac{\partial^2\mu}{\partial r^2})_{r_e}Q^2 + \ldots\ldots$$

$Q = r - r_e$

Bending

So, this we also covered. So, and this is also covered if you recall. So, we also covered what we call the Beer law. So, which takes into account that if there is an incident radiation from the left, and that it progressively gets absorbed within a medium, which has got a particular concentration of the species that absorbs the radiation. And if the radiation is kind of tuned, at tuned to that particular wavelength, then we get, what we call the absorption cross section, which is defined right over there.

And we also saw that, what will be the flux, absorption as it passes through it. So, this expression that you see over here is called basically the Beer's Law for absorption spectroscopy, basically Beer's law relates the attenuation in the intensity of incident light to the molar absorption coefficient and the concentration of the species in whatever that species N is, whatever that species is.

So, many species actually have vibrational modes, for example, water. So, in order to be IR active, the concerned molecule, we already said, IR should have a change in the dipole moment or a permanent dipole or both. So, water, for example, has lot of vibrational bangs, which are basically IR active. So, that means the transitional, the transition dipole moment or water is there.

So, the permanent dipole moment of water can be expanded in a Taylor series expansion about the internuclear separation distance. And that is exactly what you see over here Where q is basically the r minus re, that is changed from the equilibrium distance between the two nuclear and mu E is the dipole moment when the bond is in equilibrium. So, the, so there is a permanent dipole, and then there is a fluctuating dipole because of the stretching of the bonds. So, this can be as a symmetric stretch as you can see over there, or it can be symmetric stretch, or it can be some kind of a building of the molecule.

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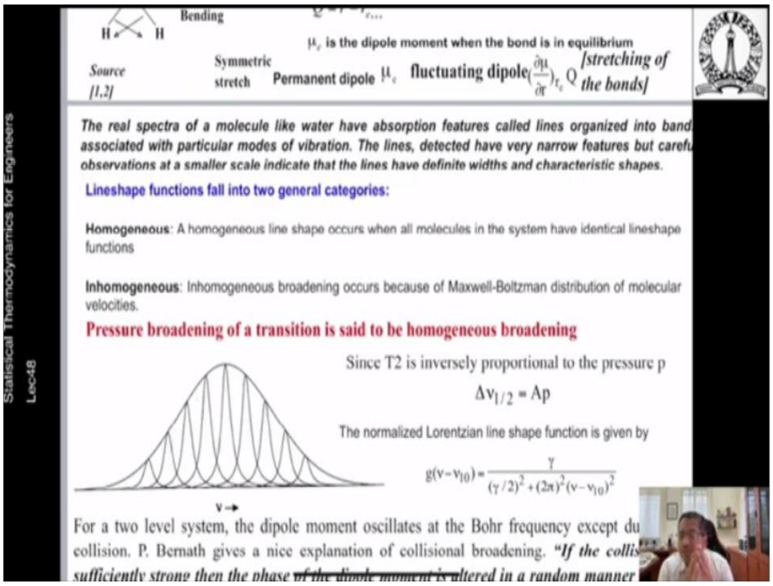
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Bending

Source [1,2]

Symmetric stretch

μ_e is the dipole moment when the bond is in equilibrium

Permanent dipole μ_e fluctuating dipole $(\frac{\partial \mu}{\partial r})_{r_e} Q$ *[stretching of the bonds]*

The real spectra of a molecule like water have absorption features called lines organized into band associated with particular modes of vibration. The lines, detected have very narrow features but carefu observations at a smaller scale indicate that the lines have definite widths and characteristic shapes.

Lineshape functions fall into two general categories:

Homogeneous: A homogeneous line shape occurs when all molecules in the system have identical lineshape functions

Inhomogeneous: Inhomogeneous broadening occurs because of Maxwell-Boltzman distribution of molecular velocities.

Pressure broadening of a transition is said to be homogeneous broadening

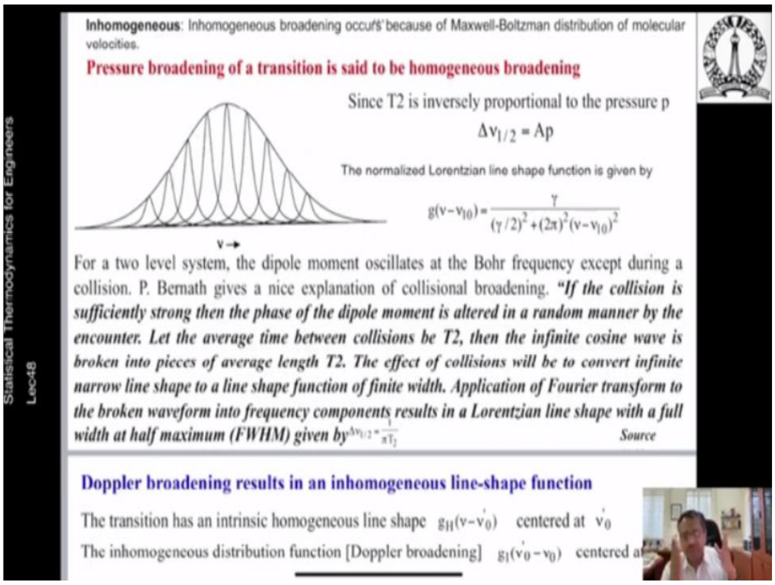
Since T2 is inversely proportional to the pressure p

$$\Delta \nu_{1/2} = Ap$$

The normalized Lorentzian line shape function is given by

$$g(\nu - \nu_{10}) = \frac{\gamma}{(\gamma/2)^2 + (2\pi)^2(\nu - \nu_{10})^2}$$

For a two level system, the dipole moment oscillates at the Bohr frequency except du collision. P. Bernath gives a nice explanation of collisional broadening. ***"If the collis sufficiently strong then the phase of the dipole moment is altered in a random manner***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Inhomogeneous: Inhomogeneous broadening occurs because of Maxwell-Boltzman distribution of molecular velocities.

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For a two level system, the dipole moment oscillates at the Bohr frequency except during a collision. P. Bernath gives a nice explanation of collisional broadening. ***"If the collision is sufficiently strong then the phase of the dipole moment is altered in a random manner by the encounter. Let the average time between collisions be T2, then the infinite cosine wave is broken into pieces of average length T2. The effect of collisions will be to convert infinite narrow line shape to a line shape function of finite width. Application of Fourier transform to the broken waveform into frequency components results in a Lorentzian line shape with a full width at half maximum (FWHM) given by*** $\Delta \nu_{1/2} = \frac{1}{\pi T_2}$ *Source*

Doppler broadening results in an inhomogeneous line-shape function

The transition has an intrinsic homogeneous line shape $g_H(\nu - \nu_0')$ centered at ν_0'

The inhomogeneous distribution function [Doppler broadening] $g_I(\nu_0' - \nu_0)$ centered a

So, the real spectra of water, if you look at it, it has absorption features for lines organized into bands, associated with a particular modes of vibration. These lines detected have very narrow features, but carefully observed at smaller time scales indicate that the lines have definite bits and characteristic shapes. So, let me see, so as you can also, we noted that the line shape functions basically fall into two categories, homogenous and inhomogeneous.

So, homogenous line shape occurs when all molecules in the system have identical line shape functions. Inhomogeneous broadening or line shapes has when the inhomogeneous broadening occurs because of Maxwell Bosman distribution of the molecule velocities. Now pressure broadening, which we already did, is said to be homogenous broadening So, pressure broadening is given by the normalized Lorentzia line shape, which you see over here.

So, for example, protein Bernath, for a two level system, the dipole moment activates a bore frequency except during acylation.

So, that the Bernath, what he is given a nice explanation of collisional broadening is that if the collision is sufficiently strong, then the phase of the dipole moment is altered in a random manner by the encounter. The average time between two collisions, if it is T2, then the, then the infinite sine wave is broken into pieces of average length of T2.

So, the effect of collision will be to convert an infinite narrow line shape to a line shape function of a finite width. So, the applica, if you apply now the Fourier transform to the broken wave for, m as you see over there in the figure, into frequency components. So, results in what we call a Lorenzien line shape width, with a full width at half maximum given that is delta half as 1 over pi by T2, where T2 is the average time between two collisions. Understand?

So, there are collision between the molecules, obviously. So, as it collides, the wave form is broken into these individual pieces, which has got an average time of T2 essentially. So, this converts it from a narrow infinite, cosine wave from an infinite cosine wave, it is broken into average pieces of length, T2.

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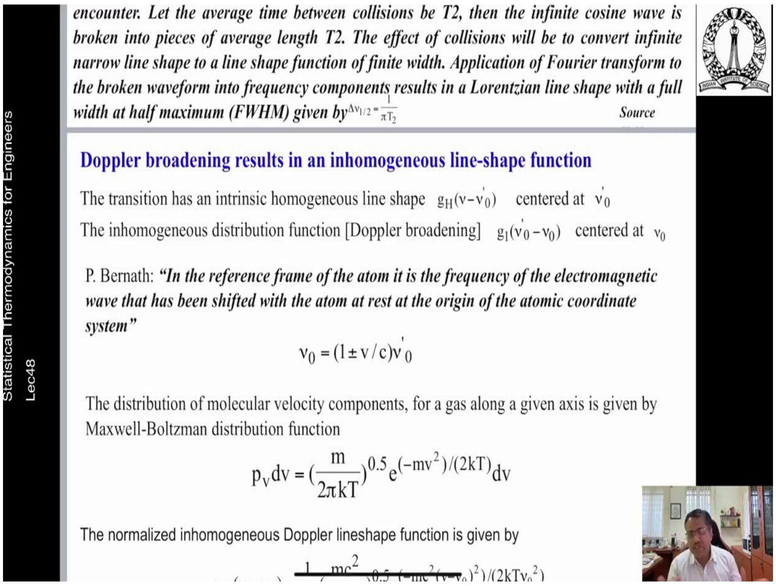


encounter. Let the average time between collisions be T2, then the infinite cosine wave is broken into pieces of average length T2. The effect of collisions will be to convert infinite narrow line shape to a line shape function of finite width. Application of Fourier transform to the broken waveform into frequency components results in a Lorentzian line shape with a full width at half maximum (FWHM) given by $\Delta\nu_{1/2} = \frac{1}{\pi T_2}$ *Source*

Doppler broadening results in an inhomogeneous line-shape function

The transition has an intrinsic homogeneous line shape $g_H(\nu - \nu_0')$ centered at ν_0'

The inhomogeneous distribution function [Doppler broadening] $g_I(\nu_0' - \nu_0)$ centered at ν_0

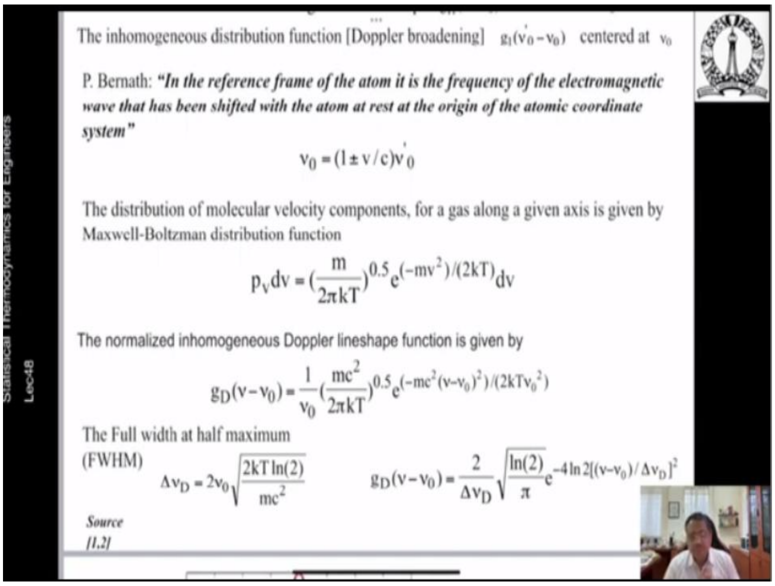
P. Bernath: ***"In the reference frame of the atom it is the frequency of the electromagnetic wave that has been shifted with the atom at rest at the origin of the atomic coordinate system"***

$$\nu_0 = (1 \pm v/c)\nu_0'$$

The distribution of molecular velocity components, for a gas along a given axis is given by Maxwell-Boltzman distribution function

$$p_v dv = \left(\frac{m}{2\pi kT}\right)^{0.5} e^{(-mv^2)/(2kT)} dv$$

The normalized inhomogeneous Doppler lineshape function is given by



The inhomogeneous distribution function [Doppler broadening] $g_I(v_0' - v_0)$ centered at v_0

P. Bernath: ***"In the reference frame of the atom it is the frequency of the electromagnetic wave that has been shifted with the atom at rest at the origin of the atomic coordinate system"***

$$v_0 = (1 \pm v/c)v_0'$$

The distribution of molecular velocity components, for a gas along a given axis is given by Maxwell-Boltzman distribution function

$$p_v dv = (\frac{m}{2\pi kT})^{0.5} e^{(-mv^2)/(2kT)} dv$$

The normalized inhomogeneous Doppler lineshape function is given by

$$g_D(v - v_0) = \frac{1}{v_0}(\frac{mc^2}{2\pi kT})^{0.5} e^{(-mc^2(v-v_0)^2)/(2kTv_0^2)}$$

The Full width at half maximum (FWHM)

$$\Delta v_D = 2v_0\sqrt{\frac{2kT\ln(2)}{mc^2}} \qquad g_D(v - v_0) = \frac{2}{\Delta v_D}\sqrt{\frac{\ln(2)}{\pi}} e^{-4\ln 2[(v-v_0)/\Delta v_D]^2}$$

Source *[1,2]*

Now the doppler, on the other hand results in an inhomogeneous line shift. So, this is the, the Lorentzian is applicable for all kinds of line shape, right? Doppler broadening, on the other hand results in what we call an inhomogeneous liner line shape function. So, this transition basically has an homogenous line shape centered around say, V naught prime. And the inhomogeneous function that is a doppler broadening is centered around V naught.

Say in the reference frame of the atom, it is a frequency of the electromagnetic wave that has been shifted with the atom at rest and the original of the atomic coordinate system So, it is definitely given by the molecular velocity components v over here, but a gas along a given axis, it is given by the Maxwell Goldsman distribution. So, the alteration in the frequency happens because of the molecular motion, because of the molecular velocity components.

So, the normalized doppler line shape is given by this, which is a Gaussian distribution as a matter of fact is pretty complicated to write. The full width at half maximum is given by this. And the total line shape function is given by what is given at the end of the table. So, the full weight, that half maximum is here, and the normalized top line shape function is given like this.

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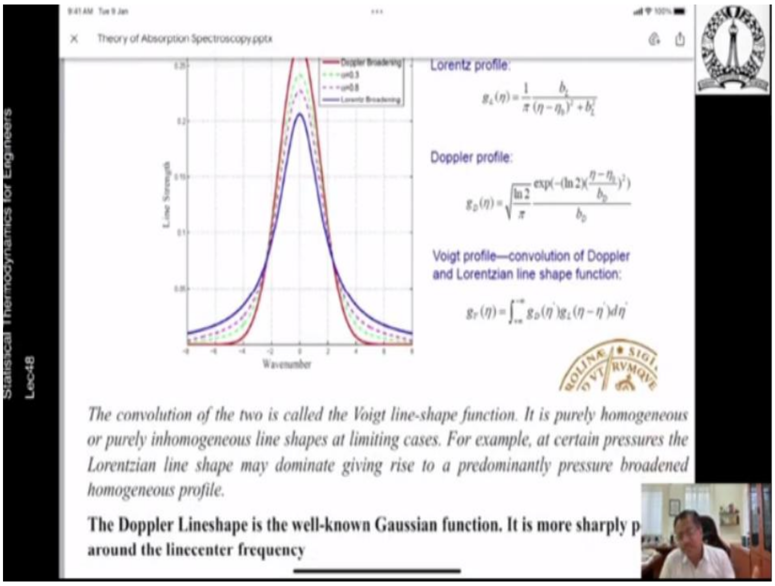


Lorentz profile:

$$g_L(\eta) = \frac{1}{\pi} \frac{b_L}{(\eta - \eta_0)^2 + b_L^2}$$

Doppler profile:

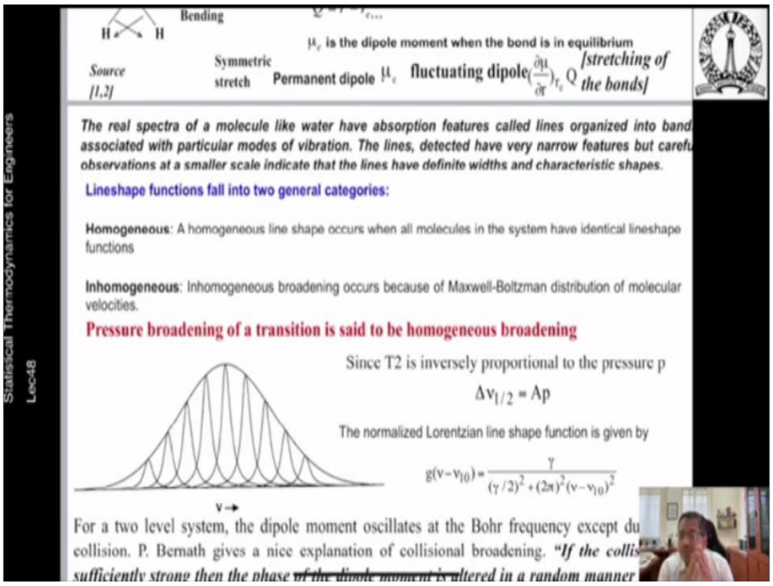
$$g_D(\eta) = \sqrt{\frac{\ln 2}{\pi}} \frac{\exp(-(\ln 2)(\frac{\eta - \eta_0}{b_D})^2)}{b_D}$$

Voigt profile—convolution of Doppler and Lorentzian line shape function:

$$g_V(\eta) = \int_{-\infty}^{\infty} g_D(\eta') g_L(\eta - \eta') d\eta'$$

The convolution of the two is called the Voigt line-shape function. It is purely homogeneous or purely inhomogeneous line shapes at limiting cases. For example, at certain pressures the Lorentzian line shape may dominate giving rise to a predominantly pressure broadened homogeneous profile.

The Doppler Lineshape is the well-known Gaussian function. It is more sharply p around the linecenter frequency



μ_e is the dipole moment when the bond is in equilibrium

Source [1,2] Permanent dipole μ_e fluctuating dipole$(\frac{\partial \mu}{\partial r})_{r_e} Q$ *[stretching of the bonds]*

The real spectra of a molecule like water have absorption features called lines organized into band associated with particular modes of vibration. The lines, detected have very narrow features but carefu observations at a smaller scale indicate that the lines have definite widths and characteristic shapes.

Lineshape functions fall into two general categories:

Homogeneous: A homogeneous line shape occurs when all molecules in the system have identical lineshape functions

Inhomogeneous: Inhomogeneous broadening occurs because of Maxwell-Boltzman distribution of molecular velocities.

Pressure broadening of a transition is said to be homogeneous broadening

Since T2 is inversely proportional to the pressure p

$$\Delta v_{1/2} = Ap$$

The normalized Lorentzian line shape function is given by

$$g(v - v_{10}) = \frac{\gamma}{(\gamma/2)^2 + (2\pi)^2 (v - v_{10})^2}$$

For a two level system, the dipole moment oscillates at the Bohr frequency except du collision. P. Bernath gives a nice explanation of collisional broadening. ***"If the collis sufficiently strong then the phase of the dipole moment is altered in a random manner***

So, if we now look at the profiles, so the Lorentz profile, if you see is a Lorentzian in origin, and you can see that it is a little wide at the base. And the doppler is more and narrower. So, the convolution of these two profile, which is called the Voigt profile, is purely homogenous or purely inhomogeneous line shapes at the limiting cases. For example, like certain pressures, the Lorentzian line shape may dominate giving rise to a predominantly pressured broadened homogenous profile.

Whereas, Lorenzen line shape, which is known, which is given by the well-known gosh distribution, it is more sharply peaked as you can see over here, it is more sharply peaked It is more sharply peaked, along the line center frequency. So, that Lorentzian line shape has a clear dominance in the far wing region. So, if you look at the wing of the distributions, so there, the Lorentzian line shape clearly dominates over the Gaussian.

So, so the understanding of it here is that whenever you have an absorption spectroscopy, let me put it this way, whenever you have a radiation on a gas or any medium where the radiation is passing from this way to that way, so, there is absorption of the radiation provided you have the frequency tube to the molecular transitions concerned. Now, normally in this case, your absorption profiles should be very sharp, it should be like a Dirac delta function, but ideally that is naught the case. Why that happens, because the molecules collide and because of the collision that we saw that the transition, which was nicely cycling, actually gets, it destroys the phase, it kind of resets the system.

So, that is what happens and that actually enlarges the line shape, the frequency width. And that is exactly what we saw when it is, when, when it is a pressure broadening, that means that the concentration is high, we have too many molecules colliding with each other, and that is resetting the system. And because of this molecular velocity, we get further broadening because of the top load effect. So, these are the two things that we should keep in mind.

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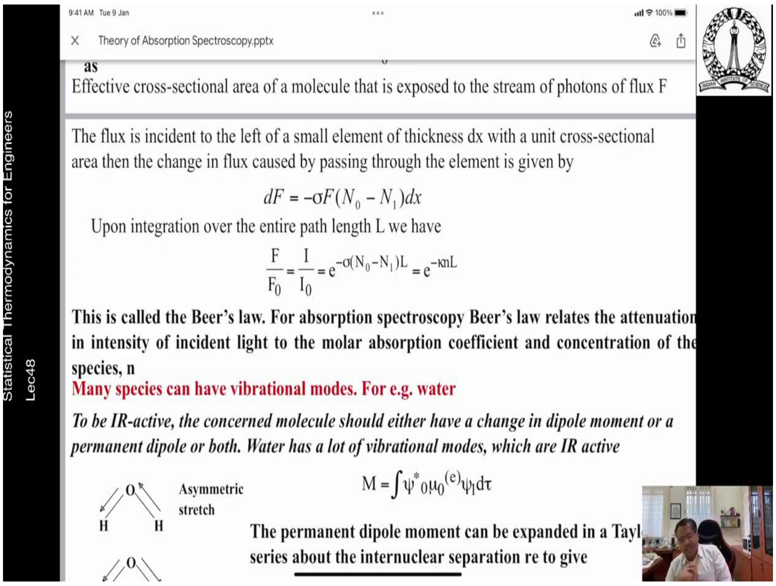

as
Effective cross-sectional area of a molecule that is exposed to the stream of photons of flux F

The flux is incident to the left of a small element of thickness dx with a unit cross-sectional area then the change in flux caused by passing through the element is given by

$$dF = -\sigma F(N_0 - N_1)dx$$

Upon integration over the entire path length L we have

$$\frac{F}{F_0} = \frac{I}{I_0} = e^{-\sigma(N_0 - N_1)L} = e^{-\kappa nL}$$

This is called the Beer's law. For absorption spectroscopy Beer's law relates the attenuation in intensity of incident light to the molar absorption coefficient and concentration of the species, n

Many species can have vibrational modes. For e.g. water

To be IR-active, the concerned molecule should either have a change in dipole moment or a permanent dipole or both. Water has a lot of vibrational modes, which are IR active

Asymmetric stretch

$$M = \int \psi^*{}_0 \mu_0{}^{(e)} \psi_1 d\tau$$

The permanent dipole moment can be expanded in a Tayl series about the internuclear separation re to give

At the same time, if we look at the final form of the Beer Lambert law, you will see that it actually, so F naught, is the, is the flux, which is incident, which is coming out and F naught is an incident flux. So, these are the two components that you can measure. So, when somebody is measuring up by absorptions spectroscopy, what do you normally do? You measure what is coming out and entering the medium, and then you measure what is coming out of the medium.

So, u know F and you know F naught that means you know the intensity that is going in versus the intensity that is coming out. So, the ratio of these two is given now by the exponential of what the absorption coefficient. And the concentration. So, if you know the absorption coefficient, you know the concentration because the lining, the total path length is also something that, that is that capital L. So, more you increase the path, greater is this I over I naught ratio. As a result of that more sensitive is your measurement. That means your error actually goes down a little bit.

And it can be done for water. As we saw that there are various molecular, molecular species which is naught vibrational modes and water being one of them, which has got a permanent and a fluctuating dipole. And that is what leads to the large number of IR active band. So, IR spectroscopy is regularly used for water.

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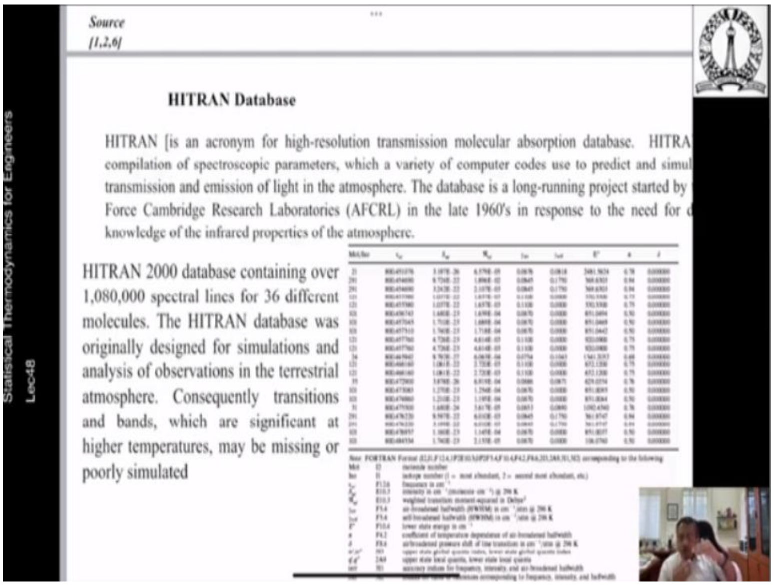

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[1,2,6]

HITRAN Database

HITRAN [is an acronym for high-resolution transmission molecular absorption database. HITRA compilation of spectroscopic parameters, which a variety of computer codes use to predict and simul transmission and emission of light in the atmosphere. The database is a long-running project started by Force Cambridge Research Laboratories (AFCRL) in the late 1960's in response to the need for knowledge of the infrared properties of the atmosphere.

HITRAN 2000 database containing over 1,080,000 spectral lines for 36 different molecules. The HITRAN database was originally designed for simulations and analysis of observations in the terrestrial atmosphere. Consequently transitions and bands, which are significant at higher temperatures, may be missing or poorly simulated

So, in this case, we use something which is called a HITRAN database. The HITRAN database is a compilation of spectroscopic parameters, where a variety of molecule computer codes are used to predict and simulate transmission and emission of light in the atmosphere. So, database is a long running project, started by four by the Air Force Cambridge Research Laboratories in the late 1960s.

So, the HITRAN database actually, is composed of over 1 million spectral lines of 36 different molecules. And if you look at it now over here, if you look at the sample table, you will see several types of air broadened half weight, self-broadened half weight, and all these parameters are listed. So, these provides the unique opportunity for us, to use this using computer simulation and theoretically predict what will be the, the spectral signatures.

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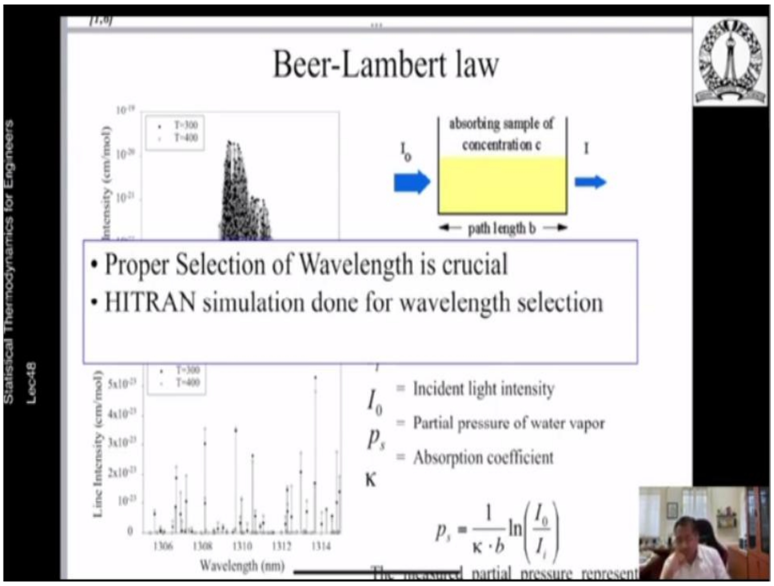


Beer-Lambert law

- Proper Selection of Wavelength is crucial
- HITRAN simulation done for wavelength selection

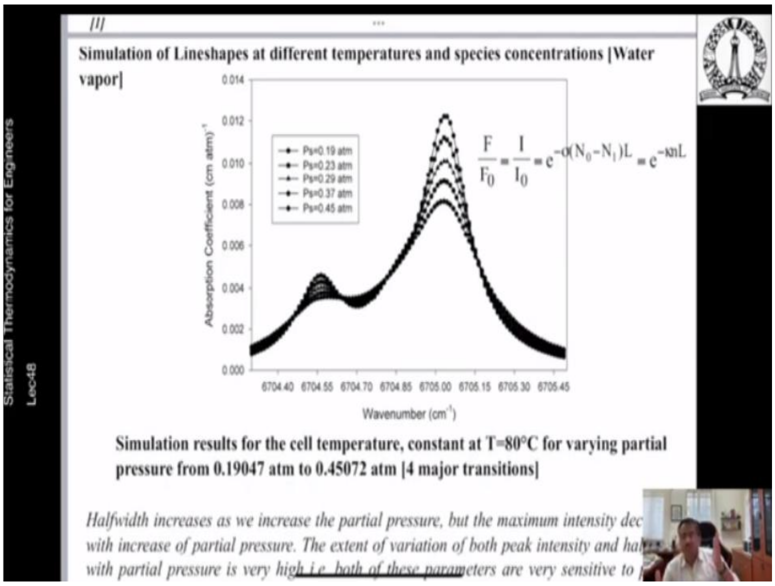
I_0 = Incident light intensity

P_s = Partial pressure of water vapor

κ = Absorption coefficient

$$p_s = \frac{1}{\kappa \cdot b}\ln\left(\frac{I_0}{I_t}\right)$$

The measured partial pressure represent



Simulation of Lineshapes at different temperatures and species concentrations [Water vapor]

$$\frac{F}{F_0} = \frac{I}{I_0} = e^{-\sigma(N_0 - N_1)L} = e^{-\kappa n L}$$

Simulation results for the cell temperature, constant at T=80°C for varying partial pressure from 0.19047 atm to 0.45072 atm [4 major transitions]

Halfwidth increases as we increase the partial pressure, but the maximum intensity dec with increase of partial pressure. The extent of variation of both peak intensity and hal with partial pressure is very high i.e. both of these parameters are very sensitive to

So, when you do actually Beer Lambert law, when you look at the, say for example the water, you see this many number of transitions at different temperatures. So, as you can see now, if you pass this through a sample, you can measure the partial pressure of the species. This partial pressure is nothing but the concentration of the species that can uniquely measured and you can simulate the line shapes at different temperatures and concentrations for water vapor, for example, this is water vapor had done at different partial pressure. So, 0.1, 9.9 atmosphere to 0.45 atmosphere.

You see the absorption coefficient versus the wave upper. You see that this is the line shape that you get. This is done by simulating it by using an actual Voigt profile. So, the simulation results for cell tempera for say water at whatever temperature, 80 degrees Celsius for different partial pressures. And in this particular wave number space, we have four major transitions.

So, here what we see the halfway increases as we increase the partial pressure of water because we increase the pollution of protein. The maximum intensity decreases with increase in partial pressure. The extent of variation of both peak intensity and halfway to partial pressure is very high. So, both of these parameters are sensitive to partial pressure. That is what we can say over here.

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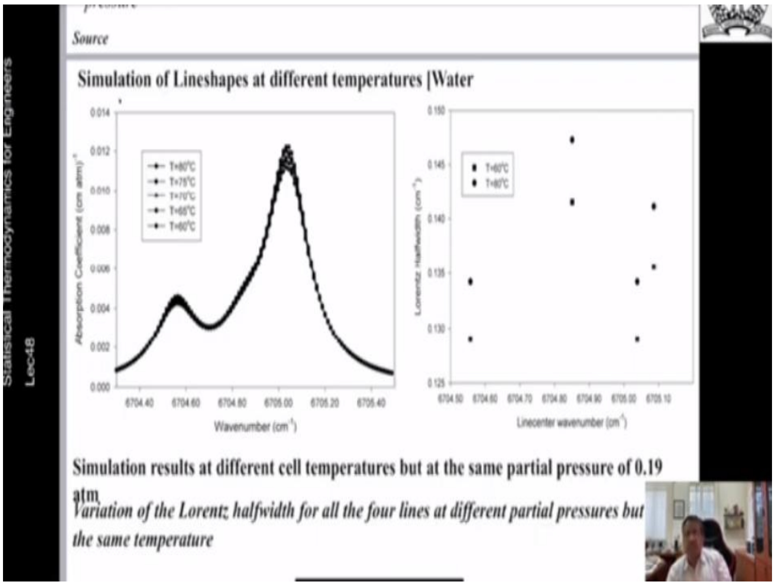

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Simulation of Lineshapes at different temperatures |Water

Simulation results at different cell temperatures but at the same partial pressure of 0.19 atm

Variation of the Lorentz halfwidth for all the four lines at different partial pressures but the same temperature

So, this is a different temperatures, for example, from 60 to 80 degrees Celsius. So, here you can see that if we see the change in the temperature, the variation of, line shapes at different temperatures. So, this is what you get. So, here the halfway does not change by that much, but well, it changes, but it does not change by that much. So, the variation of halfway with partial pressure is about 38 percent, not so much with respect to temperature.

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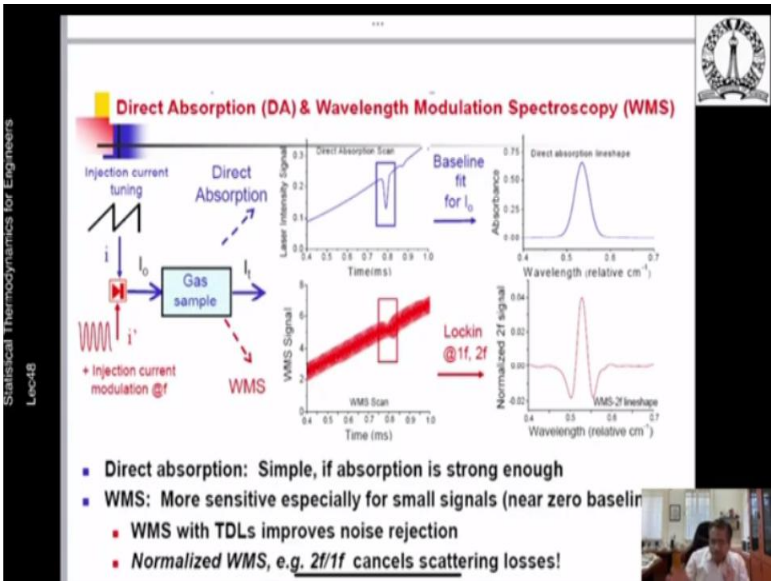

Direct Absorption (DA) & Wavelength Modulation Spectroscopy (WMS)

- Direct absorption: Simple, if absorption is strong enough
- WMS: More sensitive especially for small signals (near zero baselin
  - WMS with TDLs improves noise rejection
  - *Normalized WMS, e.g. 2f/1f cancels scattering losses!*

So, how do you measure it experimentally? So, the experimentally, you measure it by what we call a direct absorption or wavelength modulation spectroscopy. So, what happens is that you have a laser, typically a laser where you actually have a ramp function. There is the injection current tuning of the, of the laser. And then what you do is that you measure, if it is Dirac absorption, you measure what is going in, which is I naught and what is coming out, ig over here. And then you see that there is, if you measure i, you will see a blip.

So, that blip, if you kind of do the measurements, if you kind of do the processing, it will give you this kind of a distribution, which is basically nothing but absorption, direct absorption line shape function So, this is done what we call using a TDL or T-mobile diode, laser-based absorption spectroscopy. There are other variations of it, which is like wavelength modulation spectroscopy, which is kind of naught something that we are going to do in this, in this particular lecture.

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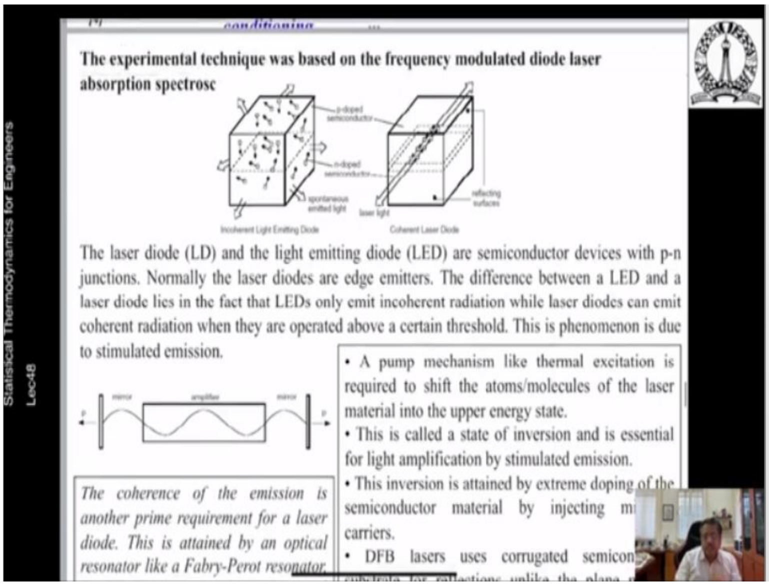
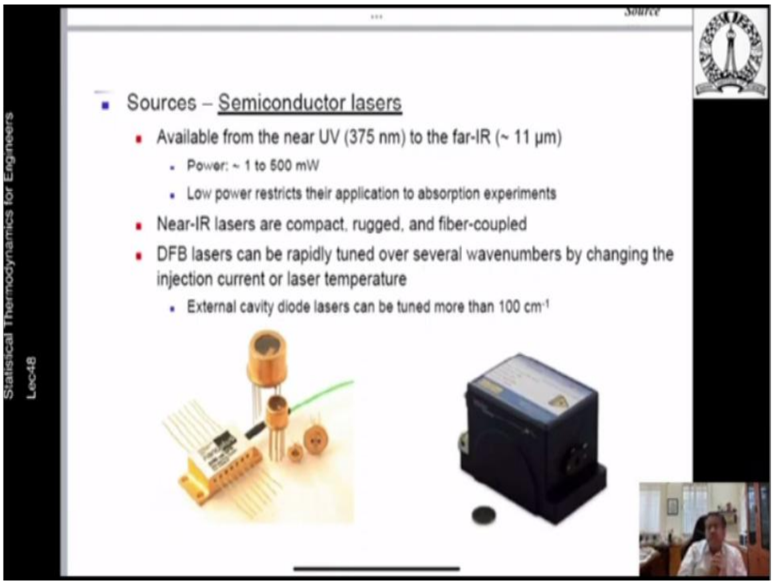


The experimental technique was based on the frequency modulated diode laser absorption spectrosc

The laser diode (LD) and the light emitting diode (LED) are semiconductor devices with p-n junctions. Normally the laser diodes are edge emitters. The difference between a LED and a laser diode lies in the fact that LEDs only emit incoherent radiation while laser diodes can emit coherent radiation when they are operated above a certain threshold. This is phenomenon is due to stimulated emission.

- A pump mechanism like thermal excitation is required to shift the atoms/molecules of the laser material into the upper energy state.
- This is called a state of inversion and is essential for light amplification by stimulated emission.
- This inversion is attained by extreme doping of the semiconductor material by injecting mi carriers.
- DFB lasers uses corrugated semicon

The coherence of the emission is another prime requirement for a laser diode. This is attained by an optical resonator like a Fabry-Perot resonator.



- Sources – Semiconductor lasers
  - Available from the near UV (375 nm) to the far-IR (~ 11 μm)
    - Power: ~ 1 to 500 mW
    - Low power restricts their application to absorption experiments
  - Near-IR lasers are compact, rugged, and fiber-coupled
  - DFB lasers can be rapidly tuned over several wavenumbers by changing the injection current or laser temperature
    - External cavity diode lasers can be tuned more than 100 cm^{-1}

So, it is usually done by a frequency modulated diode laser. So, the diode laser, if you do naught know what a diode laser is, these are semiconductor devices with PM junctions. So, normally the laser diodes are edge emitters. So, difference between an LED and a diode lies in the fact that LEDs only emit incoherent radiation, laser diodes emit coherent radiation when they are operated about the first circuit threshold.

So, and you can read about this phenomena and distributed feedback diode lasers are used for use as corrugated semi conduct substrate. So, these are all a little bit of optics, which you do not necessarily need to know. So, we are going to skip those, but these lasers are easily available in the UV and the far IR. UV and the IR lasers are very compact and rugged and fiber coupled, as you can see over here. So, they can be rapidly tuned toward several wave numbers. That is where you get that range over which you want to measure a transition. And by changing the injection current or the laser temperature, so that provides with a framework.

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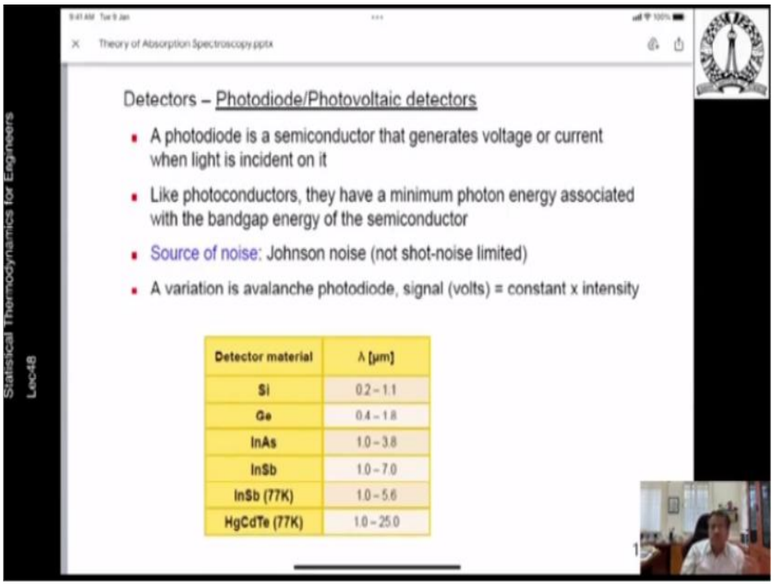

Detectors – Photodiode/Photovoltaic detectors

- A photodiode is a semiconductor that generates voltage or current when light is incident on it
- Like photoconductors, they have a minimum photon energy associated with the bandgap energy of the semiconductor
- Source of noise: Johnson noise (not shot-noise limited)
- A variation is avalanche photodiode, signal (volts) = constant x intensity

Detector material	λ [μm]
Si	0.2 – 1.1
Ge	0.4 – 1.8
InAs	1.0 – 3.8
InSb	1.0 – 7.0
InSb (77K)	1.0 – 5.6
HgCdTe (77K)	1.0 – 25.0

Now the, to detect the radiation, you use either photodiode or photovoltaic detectors. So, photodiode is a semiconductor device that generates voltage or current when light is incident on it, like photoconductors, they have a minimum photon energy associated with the band gap energy of the semiconductor. So, variation. So, there are variations of photodiodes, which once again is something that you can read.

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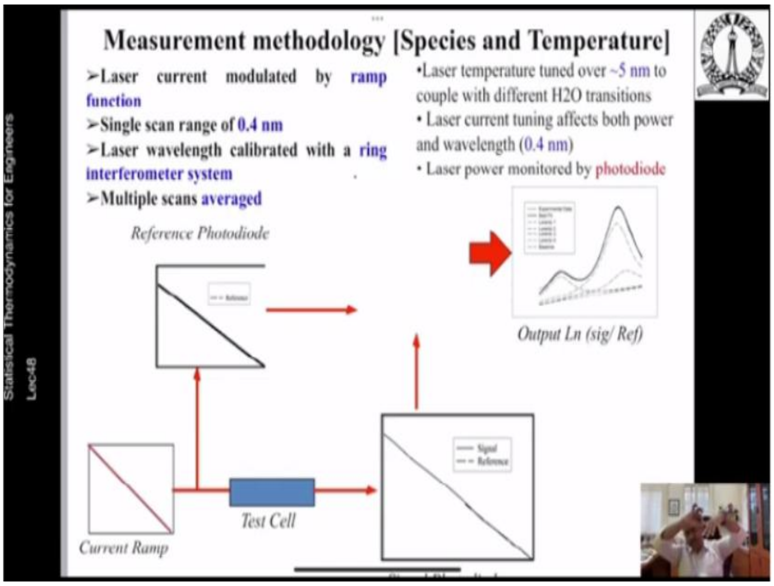

Measurement methodology [Species and Temperature]

- ➢Laser current modulated by ramp function
- ➢Single scan range of 0.4 nm
- ➢Laser wavelength calibrated with a ring interferometer system
- ➢Multiple scans averaged

- •Laser temperature tuned over ~5 nm to couple with different H2O transitions
- • Laser current tuning affects both power and wavelength (0.4 nm)
- • Laser power monitored by photodiode

So, this is how this is done. The laser current is modulated by a ramp function. Scan range is typically about 0.4 nanometres. So, very short. The laser wavelength is calibrated usually using a ring interferometer that what is the absolute wavelength at which it starts. Multiple scans are therefore average. So, this is very fast. You can do it very fast. So, what happens is that you have a reference signal.

So, you basically take the output of the laser diode, split it into two, 50-50 almost, one you pass it through the test cell, which contains the species that you want to measure. And the other is passed through a photodiode, which measures that what is I naught basically. So, once it comes out through the test cell, then you use another photodetector or photodiode to measure Ii. So, and then you plot one on the top of the other, and then you take the re ratio output is that signal by reference. So, I over I naught and basically you get this kind of align shift that you see over here.

So, this now tells you that once you plot this spectrum, this is now represented by not one transition, but several transition. In this case, there are about 4 transitions, that you can do. So, this actually, by measuring the change in this line shape, you can measure what is the partial pressure and what is the temperature. So, how do you, as you already saw that these profiles actually change quite a bit; if you look at it here, quite a bit with respect to concentration. So, if you increase the concentration, the half increases.

So, basically you are measuring this line shape using that I over I naught ratio. So, this I over I naught ratio using this, you are precisely measuring that. Now, you already know if you have recalibrated this, you already know for known concentration what is the half width, and then you use that over here to calculate the any unknown concentration that you might encounter.

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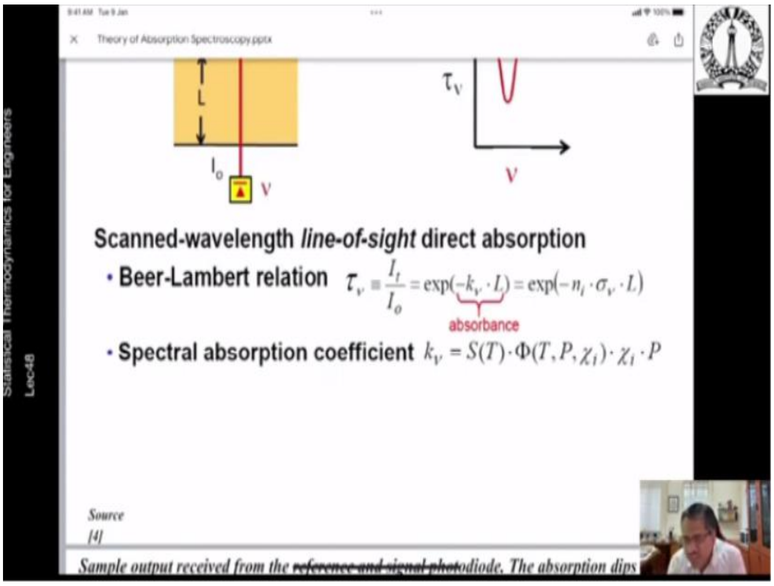
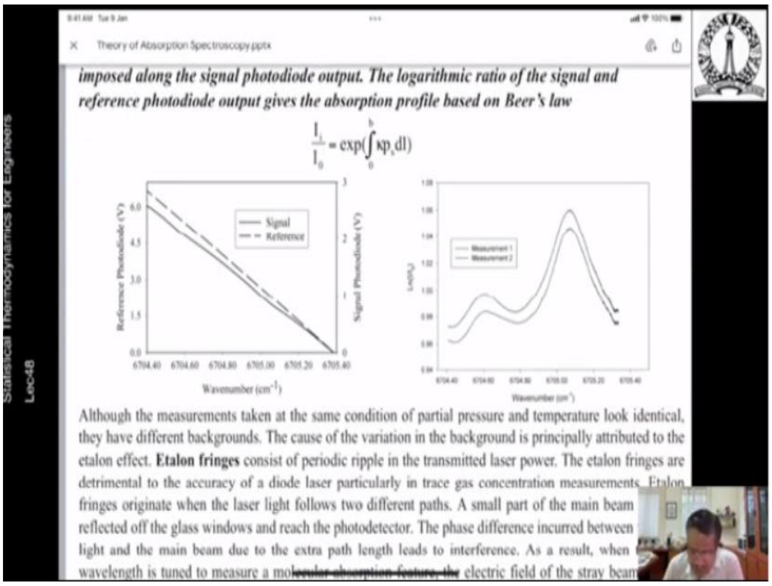


Scanned-wavelength *line-of-sight* direct absorption

- Beer-Lambert relation $\tau_\nu \equiv \frac{I_t}{I_0} = \exp(\underbrace{-k_\nu \cdot L}_{\text{absorbance}}) = \exp(-n_i \cdot \sigma_\nu \cdot L)$
- Spectral absorption coefficient $k_\nu = S(T) \cdot \Phi(T, P, \chi_i) \cdot \chi_i \cdot P$

Source
[4]

Sample output received from the ~~reference and signal photo~~diode. The absorption dips



imposed along the signal photodiode output. The logarithmic ratio of the signal and reference photodiode output gives the absorption profile based on Beer's law

$$\frac{I_t}{I_0} = \exp\left(\int_0^b \kappa p_i dl\right)$$

Although the measurements taken at the same condition of partial pressure and temperature look identical, they have different backgrounds. The cause of the variation in the background is principally attributed to the etalon effect. **Etalon fringes** consist of periodic ripple in the transmitted laser power. The etalon fringes are detrimental to the accuracy of a diode laser particularly in trace gas concentration measurements. Etalon fringes originate when the laser light follows two different paths. A small part of the main beam reflected off the glass windows and reach the photodetector. The phase difference incurred between light and the main beam due to the extra path length leads to interference. As a result, when wavelength is tuned to measure a mo~~lecular absorption feature, the~~ electric field of the stray beam

So, this is the line of site-based direct absorption. So, it has to come out, so it is averaged over the distance l, remember that distance l that is over the distance over which we have kind of averaged it out. So, and it is the log algorithmic ratio. So, you can see the two different measurements, for example, they look very identical. The base is sometimes shifted, but that is not a problem. You can just move it up and down. So, that is naught an issue at all.

So, they look, although the measurements are the same condition of partial pressure and temperature look identical, they can have different backgrounds. So, this difference in variation in background is can be attributed to something called an Etalon effect. So, Etalon fringes and periodic ripples can appear. So, these are all things that, you need to take care when you do a measurement.

So, one is theory and one is when you actually execute it. So, the execution always involves unfortunate effects, like for example, the Etalon fringes. All these things appear and you have to kind of, take care of that. So, wavelength modulation we are going to, going to avoid. So, we that is not within the scope.

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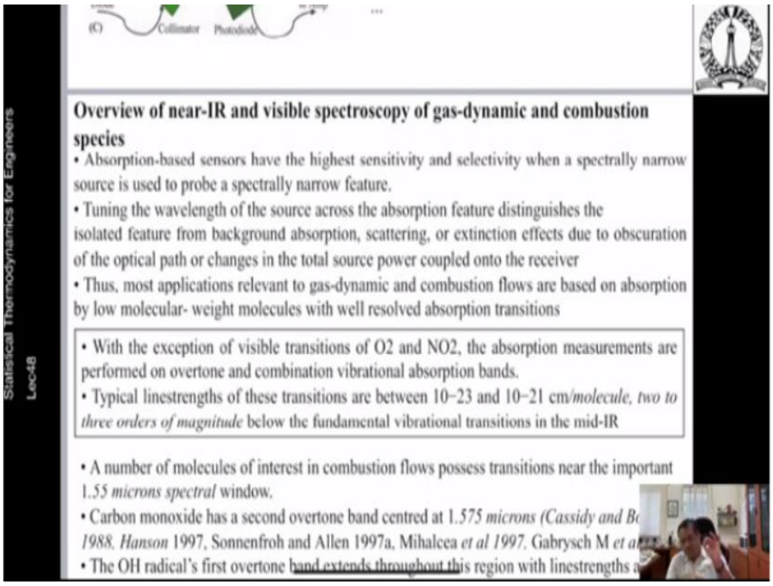

Overview of near-IR and visible spectroscopy of gas-dynamic and combustion species

- 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 B*
1988, Hanson 1997, Sonnenfroh and Allen 1997a, Mihalcea *et al 1997,* Gabrysch M *et a*
- The OH radical's first overtone band extends throughout this region with linestrengths

So, near-IR and visible spectroscopy, absorption-based sensors therefore have highest sensitivity and selectivity because of that extremely narrow spectral source that we use. So, tuning that, you can tune the wavelength to whatever transition features that you want, and that from that you can isolate what will be the concentrations or the temperature.

So, most applications relevant to gas dynamic and combustion flows are based on absorption by low molecular weight molecules with well resolved absorption transitions. So, the way the exception of visible transitions of O2 and NO2, the absorption measurements are performed on overtone and combination of vibrational absorption bands. So, typical line strengths of these absorptions are between, 10 to 20 centimetre per molecule. So, the number of, molecules of interest in combustion flows, possessed transitions near this 1.55-micron windows. So, there are a lot of these measurements are quite easily available.

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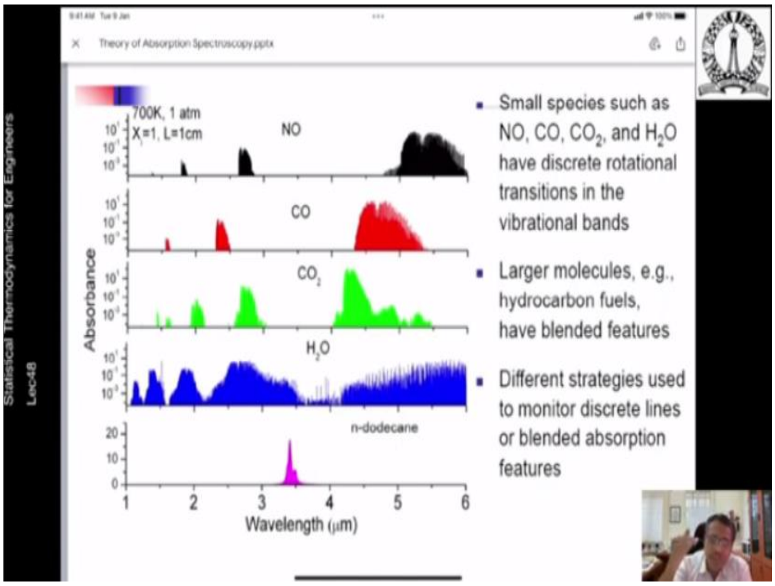

- Small species such as NO, CO, CO_2, and H_2O have discrete rotational transitions in the vibrational bands
- Larger molecules, e.g., hydrocarbon fuels, have blended features
- Different strategies used to monitor discrete lines or blended absorption features

The small species, you can, you see they have discrete rotational transitions in the vibrational bands. Larger molecules have blended features. So, all these are absorbent of NO, CO, CO2, water, and that last one is in total.

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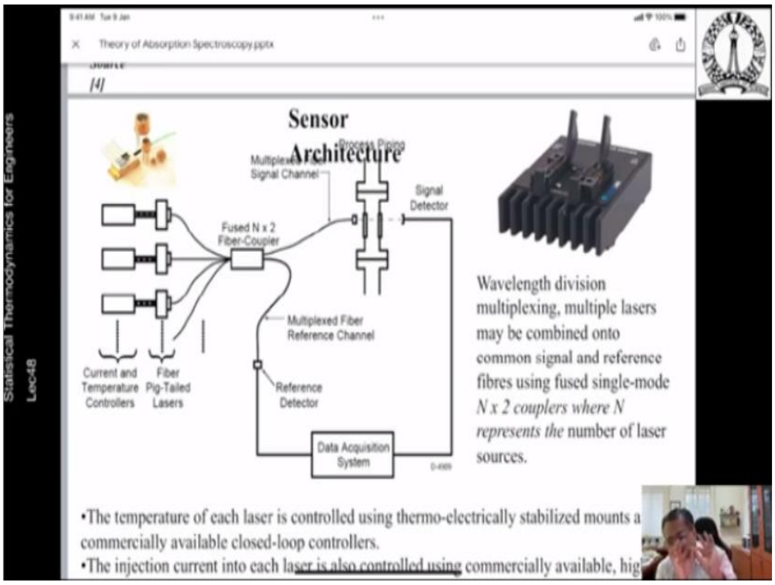
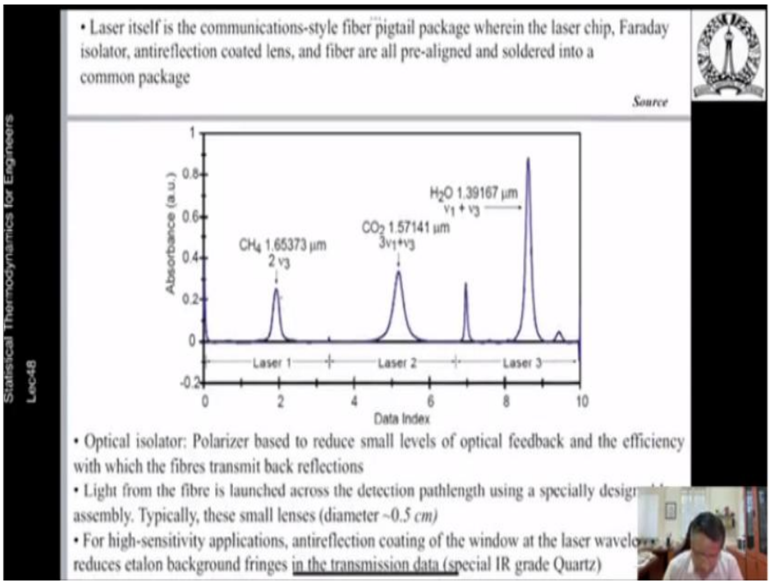


Sensor Architecture

Wavelength division multiplexing, multiple lasers may be combined onto common signal and reference fibres using fused single-mode *N x 2 couplers where N represents the* number of laser sources.

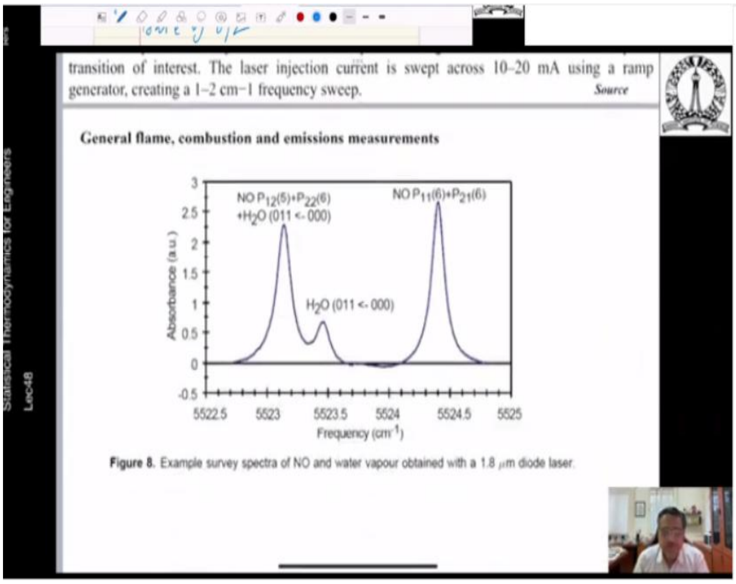
- The temperature of each laser is controlled using thermo-electrically stabilized mounts a commercially available closed-loop controllers.
- The injection current into each laser is also controlled using commercially available, hig



- Laser itself is the communications-style fiber pigtail package wherein the laser chip, Faraday isolator, antireflection coated lens, and fiber are all pre-aligned and soldered into a common package

Source

- Optical isolator: Polarizer based to reduce small levels of optical feedback and the efficiency with which the fibres transmit back reflections
- Light from the fibre is launched across the detection pathlength using a specially desig assembly. Typically, these small lenses (diameter ~0.5 *cm)*
- For high-sensitivity applications, antireflection coating of the window at the laser wavelo reduces etalon background fringes in the transmission data (special IR grade Quartz)



transition of interest. The laser injection current is swept across 10–20 mA using a ramp generator, creating a 1–2 cm−1 frequency sweep.

Source

General flame, combustion and emissions measurements

Figure 8. Example survey spectra of NO and water vapour obtained with a 1.8 μm diode laser.

So, you can also have, a complete sensor architecture in which you can have different lasers which are coupled, fused and then so the beam that comes out of it has got combination of all these wavelengths, and then it is passed through your experimental setup, which is shown right over here. And then you detect the signal and then you again, different, you can measure all species at one particular go multiple species at one particular go.

So, the laser itself is like a communication style fiber pigtail package. So, this is not a problem, and this is something that you get something like this from laser 1, laser 2, laser 3. CH4 is methane, CO2 and water. So, so these kind of measurements can be performed and then there can be also other kind of measurements like, flame and combustion emission measurements are also done.

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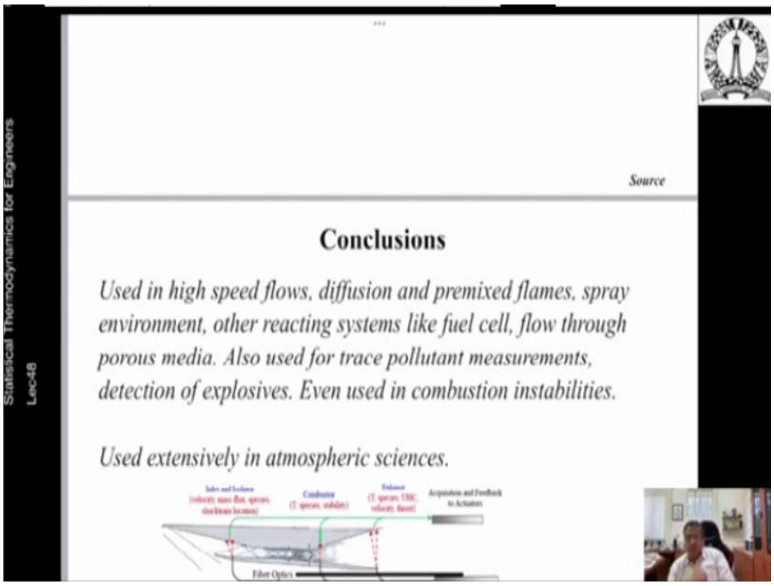

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Source

Conclusions

Used in high speed flows, diffusion and premixed flames, spray environment, other reacting systems like fuel cell, flow through porous media. Also used for trace pollutant measurements, detection of explosives. Even used in combustion instabilities.

Used extensively in atmospheric sciences.

So, used in, this is used in high speed flows, diffusion, premix, flames, spray environment, reacting systems like fuel cell, flow through porous media, also used as trace for pollutant measurements, detection of explosives of the airports. So, even used in combustion instability, it is extensively used in atmospheric sciences. So, all these things are something that that is done through absorptions spectroscopy, which is rather easy.

So, we saw how an Einstein with a two-level system, how we can, do the math and we can show exactly what will be the line shape functions, what are the forms of the line shape functions, why the line shape functions actually exist, and how the line shape functions actually respond to partial pressure and temperature.

So, with this, I think we finish the spectroscopy part of this course. There will be tutorials that will be there, there will be also a small tutorial on laser induced fluorescence, which will be the concluding part of this particular lecture. So, this basically concludes, some of the lecture portions of this particular statistical thermodynamic course. Thank you so much.