Chapter

2.7

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Alright everyone, welcome back to Phys 608, Laser Spectroscopy. Today, we embark on a crucial section of our course, Chapter 2.7, where we'll delve into the fundamental concepts of **Absorption and Emission Spectra**. These processes are at the very heart of how light interacts with matter, and understanding them quantitatively is paramount for everything we'll discuss in laser spectroscopy.

These slides were originally prepared by Distinguished Professor Doctor M. A. Gondal, for this course at KFUPM.

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So, let's lay out our **Road-Map for Section 2.7**.

Our primary **section goal** is to build a rigorous, quantitative understanding of how atoms and molecules exchange energy with light. This energy exchange, as you know, is the basis of all spectroscopy. We'll be focusing on three key processes:

1. **Absorption:** This is where an atom or molecule takes in energy from the light field, causing it to transition to a higher energy state. Think of it as the system "eating" a photon.

2. **Spontaneous emission:** An excited atom or molecule can relax to a lower energy state by itself, emitting a photon in the process. This is the basis for fluorescence and phosphorescence, and it happens, as the name suggests, spontaneously, without external coaxing from a light field.

3. **Stimulated emission:** This is the process that is absolutely key to laser operation. An already excited atom or molecule is stimulated by an incoming photon to emit a *second* photon. Crucially, this emitted photon is identical in phase, frequency, direction, and polarization to the stimulating photon. This leads to light amplification.

To achieve this understanding, we will be introducing several important tools and concepts today.

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Continuing with the tools we'll introduce and work with in this section:

* First, we'll touch upon **Spectral line observation with a dispersive spectrograph.** This is the experimental starting point – how do we actually see these spectra? We'll look at the basic principles of how a spectrograph works to separate light into its constituent wavelengths, allowing us to observe these lines.

*Next, and this is theoretically central, are the **Einstein A and B coefficients.** These coefficients, introduced by Albert Einstein, provide a quantum mechanical description of the probabilities of spontaneous emission (A coefficient), and stimulated absorption and emission (B coefficients). They are the* microscopic* parameters that govern these transition rates.

* Then we'll define the **Absorption cross section, denoted as** σ_{ik}. This is an incredibly useful quantity. It represents the effective area that an atom or molecule presents to an incoming photon for an absorption event to occur between an initial state 'i' and a final state 'k'. While related to the B coefficient, the cross-section is often more convenient in practical calculations, especially when dealing with beam intensities.

* Closely related is the **Oscillator strength, denoted** f_{ik}. This is a dimensionless quantity that measures the "strength" of a transition. It essentially compares the quantum mechanical transition probability to that of a classical electron oscillator. It's another way to quantify how strongly a particular transition interacts with light.

* Finally, we'll introduce the **Line-strength integral,** S_{ik}. This is the absorption cross section integrated over the entire frequency range of the spectral line. It

gives a measure of the total absorption strength of a line, irrespective of its shape or broadening.

These concepts are interconnected, and we'll see how they build upon each other.

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This diagram provides a nice visual overview of how these concepts fit together, forming the backbone of our understanding.

At the very top, we have **Spectral Line Observation (using a Dispersive Spectrograph)**. This represents the experimental reality, the data we collect. These observations provide the experimental basis that motivates and validates our theoretical framework.

From these observations, and from fundamental quantum theory, we develop the concept of **Einstein A and B Coefficients**. These are described as "Microscopic Transition Probabilities," which is precisely what they are – they quantify the intrinsic likelihood of an atom or molecule undergoing absorption, spontaneous emission, or stimulated emission.

Now, look at the arrows. The Einstein coefficients, particularly the B coefficient for absorption, lead to the definition of the **Absorption Cross Section,** σ_{ik}. This cross section, as we said, is that effective target area. The Absorption Cross Section, when integrated over the frequency of the line, yields the **Line-Strength Integral,** S_{ik}. This integral gives us a total measure of the line's ability to absorb light.

Going back to the Einstein A and B coefficients, they are also related to, and help define, the **Oscillator Strength,** f_{ik}. The oscillator strength is another way to characterize the intrinsic strength of a transition, and it's, as the diagram indicates, interrelated with the Absorption Cross Section. In fact, we'll see that the integrated cross-section is directly proportional to the oscillator strength.

And as the arrows converging at the bottom show, all of these concepts – experimental observation, microscopic probabilities, cross sections, oscillator strengths, and line strengths – **all contribute to** our **Section Goal**: to build that rigorous, quantitative understanding of how atoms and molecules exchange energy with light via those three fundamental processes:

1. Absorption 2. Spontaneous Emission 3. Stimulated Emission

So, this flow chart gives you a sense of the logical progression and the interplay between experiment and theory, and between different quantitative measures, that we'll be exploring.

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Now, let's clarify some **Core Definitions concerning Emission versus Absorption spectra**.

First, an **Emission spectrum**: This is defined as the spectral distribution of radiant power that *leaves a source*. So, if you have a sample that is excited – perhaps it's hot, or it's undergoing a chemical reaction, or it's being excited by a laser – it will emit light. If you disperse that light using a spectrograph and measure the intensity at each wavelength or frequency, you get its emission spectrum. It tells you what colors, or more generally, what frequencies of light the source is giving off, and how intensely.

Second, an **Absorption spectrum**: This is defined as the *difference* between the incident and transmitted spectra after light traverses a sample. Imagine you have a light source that produces a continuous range of frequencies. You pass this light through your sample. If the sample absorbs certain frequencies, then the light that comes out (the transmitted light) will have those frequencies missing or reduced in intensity. The absorption spectrum essentially highlights these "missing pieces." It's often plotted as absorbance or transmittance versus wavelength or frequency.

Now, we can talk about **Two spectral morphologies**, or shapes, that these spectra can take:

* The first is **Continuous**, meaning there are no gaps in the spectrum; it's a smooth distribution of intensity across a range of frequencies. The classic example given here is **black-body radiation**. A hot, dense object, like the filament of an incandescent light bulb or, to a good approximation, a star, emits a continuous spectrum. This arises because in such condensed matter, there's a near-continuum of available energy states and transitions.

* The second morphology is **Discrete**, which means the spectrum consists of a set of sharp lines. These lines appear at very specific frequencies. This type of spectrum arises from **quantised bound-bound transitions**. This is characteristic of isolated atoms or molecules in the gas phase. Because the energy levels within an atom or molecule are quantized (they can only take on discrete values), transitions between these levels involve the absorption or emission of photons with very specific energies, and therefore very specific frequencies, leading to these sharp lines. This is the domain where much of high-resolution laser spectroscopy operates.

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Before we delve deeper into the equations, let's highlight a **Key physical constant that will appear throughout our discussions**: This is, of course, the **Planck constant, denoted by 'h'**.

Its value is approximately $h = 6.626 \times 10^{-34}$ J s (that's J s).

Planck's constant is truly fundamental to quantum mechanics. It's the proportionality constant that relates the energy of a photon to its frequency, through the famous equation $E = h\nu$. Max Planck introduced this constant in

1900 to solve the ultraviolet catastrophe in black-body radiation, by postulating that energy is quantized in units of $h\nu$. Its appearance in virtually all spectroscopic equations underscores the quantum nature of light-matter interactions.

We'll also frequently encounter 'h-bar', which is $\frac{h}{2\pi}$, often called the reduced Planck constant, especially when working with angular frequencies.

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Let's now consider **Discrete Transition Energetics**. This is fundamental to understanding line spectra.

* We start by considering a simplified model: **one atom or molecule with two stationary (bound) states.** We'll label these states using Dirac notation: the initial state as ket $|i\rangle$ (that's $|i\rangle$), with energy E_i, and the final state as ket $|k\rangle$ (that's $|k\rangle$), with energy E_k. We'll assume that the state $|k\rangle$ is higher in energy than state $|i\rangle$, so E_k is greater than E_i. This setup is the basis for absorption from i to k, or emission from k to i.

* The cornerstone here is the **Energy-frequency relation**, often called the Planck-Einstein relation or the Bohr frequency condition. It states that for a transition to occur between these two states via the absorption or emission of a single photon, the photon's energy, $h\nu_{ik}$, must exactly match the energy difference between the two states:

$$h\nu_{ik} = E_\mathrm{k} - E_\mathrm{i}$$

Here, ν_{ik} is the frequency of the photon involved in the transition between states i and k. This can be rearranged to solve for the frequency:

$$\nu_{ik} = \frac{E_\mathrm{k} - E_\mathrm{i}}{h}$$

This equation is absolutely central. It tells us that the frequency of light absorbed or emitted is directly determined by the energy spacing of the quantum states of the atom or molecule. This is why spectroscopy is such a powerful tool for probing atomic and molecular structure – by measuring the frequencies of spectral lines, we can determine the energy level differences.

* Another quantity often used in spectroscopy is the **Wavenumber, denoted as** $\tilde{\nu}_{ik}$. It is defined as the reciprocal of the wavelength λ_{ik}:

$$\tilde{\nu}_{ik} = \frac{1}{\lambda_{ik}}$$

Wavenumbers are very convenient, especially in infrared spectroscopy. The units are typically **inverse centimeters (**cm^{-1}). Since energy is proportional to frequency ($E = h\nu$) and frequency is c/λ, energy is also proportional to wavenumber ($E = hc\tilde{\nu}$). So, wavenumbers provide a direct measure of energy, and the numbers are often of a convenient magnitude, say, hundreds to thousands of inverse centimeters for vibrational transitions.

Now for some basic **Terminology** related to these concepts:

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Continuing with our terminology:

* When we speak of a spectral **"Line"**, this corresponds to a transition involving a single, well-defined frequency ν_{ik} or, equivalently, a single wavelength λ_{ik}. This arises from a transition between two specific quantum states, as dictated by the energy-frequency relation we just discussed. In an ideal world, this line would be infinitely sharp, but as we'll see, lines always have some finite width due to various broadening mechanisms.

* Often, we observe not just isolated lines, but a **"Multiplet" or a "Band"**. These terms refer to a **cluster of related lines**. These clusters arise when an energy level is actually composed of several closely spaced sub-levels. * For

example, **fine structure** splitting, which gives rise to multiplets, is due to the interaction between the electron's spin and its orbital angular momentum. The sodium D-lines we'll discuss are a classic example of a fine-structure doublet. * **Hyperfine structure** results in even smaller splittings, due to the interaction of the total electronic angular momentum with the nuclear spin. These require very high-resolution spectroscopy to observe. * In molecules, we also have **vibrational bands**, where a single electronic transition is accompanied by changes in the vibrational quantum number, leading to a series of closely spaced lines corresponding to different vibrational transitions (e.g., P, Q, R branches in rovibrational spectra).

Understanding this terminology is key to describing and interpreting the spectra we observe.

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Now let's turn to the practical aspect of **How a Spectrograph Separates Wavelengths**. This slide outlines the basic **Optical Path** in a typical dispersive spectrograph.

1. First, light from the source enters through an **Entrance slit, labeled S**. This slit serves to **define a spatially narrow source**. The width of this slit is critical; a narrower slit generally leads to better spectral resolution (the ability to distinguish closely spaced wavelengths), but it also reduces the amount of light entering the instrument, which can affect signal-to-noise. The slit essentially creates a series of line images at the detector, one for each wavelength.

2. Next, the diverging light from the slit encounters **Collimating optics**. These are typically a lens or a curved mirror. Their purpose is to take the diverging light rays and make them parallel, creating a **parallel beam** or collimated beam. This is important because dispersive elements like diffraction gratings work best with collimated light.

3. The collimated beam then strikes the **Dispersive element**. This is the heart of the spectrograph. It can be a **prism** or, more commonly in modern instruments, a **diffraction grating**.

* A prism works based on the principle that the refractive index of the prism material varies with wavelength (dispersion). Different wavelengths are bent by slightly different angles.

* A diffraction grating has a series of closely spaced grooves. It separates wavelengths based on diffraction and interference; the angle at which a particular wavelength is diffracted depends on the wavelength itself according to the grating equation. The key outcome is that the dispersive element **introduces an angle-wavelength dependence**: different wavelengths emerge from it at different angles.

4. Finally, these angularly separated beams of different wavelengths pass through a **Camera lens** (or another curved mirror, often called a focusing optic). This lens **refocuses each wavelength to a different horizontal coordinate in the focal plane, labeled B**, where the detector is placed. So, you get a spatial separation of wavelengths – red light might be focused at one position on the detector, blue light at another.

This sequence of operations allows the spectrograph to spread out the light into its spectrum.

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So, after the light has traversed the optical path of the spectrograph, what does the **Detector see**? This depends on the nature of the light source.

* If you have a **Continuous source** – like an incandescent bulb, which emits light over a broad, unbroken range of wavelengths – the detector will see a **bright rainbow band**. Each wavelength is focused to a slightly different

position, and because all wavelengths are present, these images merge into a continuous smear of color (if in the visible) or intensity.

* On the other hand, if you have a **Discrete source** – like a gas discharge lamp (e.g., a mercury lamp or a sodium lamp) which emits light only at specific, characteristic wavelengths – the detector will see a **series of bright "line" images of the slit**. Each specific wavelength present in the source forms a distinct, sharp image of the entrance slit at a particular position on the detector. These are the spectral lines we've been talking about.

This distinction is fundamental to interpreting what you observe with a spectrograph.

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Here we have a diagram illustrating a very common type of spectrograph, the **Czerny-Turner Spectrograph**, shown in a plan view (looking down from above). Let's trace the light path and identify the components, which correspond to the general steps we just discussed.

1. Light enters through the **Entrance Slit**, labeled 'S' on the left. This is where our light source is effectively defined.

2. The light diverging from the slit strikes the first curved mirror, **M1**, which is the **Collimation mirror**. As you can see from the rays drawn, M1 reflects the light and makes the rays parallel before they reach the next component.

3. The collimated beam then illuminates the **Dispersion element**, which in a Czerny-Turner design is typically a **diffraction grating**, labeled 'G'. The grating is shown tilted. As the light reflects off the grating, different wavelengths are diffracted at different angles. The diagram shows two representative wavelengths, λ_1 (red rays) and λ_2 (blue rays), emerging from the grating at distinct angles.

4. These angularly separated beams then travel to a second curved mirror, **M2**, which is the **Focusing mirror**. M2 takes these diverging (in angle) beams and focuses them down.

5. Finally, the light is focused onto the **Detector plane**, labeled 'B'. Notice how λ_1 and λ_2 are now focused at different spatial positions on this plane. This is where you would place a CCD camera, a photodiode array, or historically, a photographic plate, to record the spectrum. The label "5. Detection (B)" indicates this.

The Czerny-Turner configuration is popular because it uses mirrors, which minimizes chromatic aberration (wavelength-dependent focusing issues that lenses can have), and it provides good image quality over a relatively wide focal plane. The separation between λ_1 and λ_2 on the detector depends on the grating's dispersion and the focal length of M2.

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Now we come to a critical performance characteristic of any spectrograph: its **Resolving Power Requirement**.

* **Resolving power,** R, is formally defined as the wavelength, λ, divided by the smallest difference in wavelength, $\Delta\lambda$, that can just be distinguished or resolved: R is identically equal to $\frac{\lambda}{\Delta\lambda}$. A higher resolving power means the instrument can distinguish between two spectral lines that are very close together in wavelength. For example, if R is 1000, at a wavelength of 500 nanometers, you can resolve features that are 0.5 nanometers apart. If R is $100{,}000$, you can resolve features 0.005 nanometers apart at the same wavelength.

* So, **To observe distinct lines**, especially if they are close together, the resolving power R of your spectrograph must be significantly greater than the ratio of the line's central wavelength, λ_{ik}, to the intrinsic width of the spectral

line itself. This intrinsic width could be the **natural linewidth** (due to the lifetime of the excited state) or the **Doppler width** (due to the thermal motion of the atoms or molecules), or a combination. The condition is written as: R must be much greater than $\frac{\lambda_{ik}}{\text{natural/Doppler width}}$. If your instrument's R doesn't meet this condition for a given pair of lines, you won't be able to tell them apart.

* Consequently, **If** R is insufficient, adjacent lines blur together into an apparent continuum or a single, broader feature. You lose the information that there were actually multiple distinct transitions.

* It's interesting to note the behavior for different types of spectra: * **Continuous spectra remain continuous even for** R approaching ∞. A truly continuous source, like an ideal black body, will always look continuous, no matter how good your spectrograph is. Higher resolution just confirms its continuous nature. * **Discrete spectra, however, become a set of** δ-function-like peaks as R approaches ∞. In the ideal limit of perfect resolution and no intrinsic line broadening, each spectral line would be infinitely sharp, appearing as a Dirac delta function at its precise frequency. Real lines always have some width, but the better the R, the sharper they appear.

So, choosing a spectrograph with adequate resolving power is crucial for the specific spectroscopic task at hand.

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Let's now discuss the **Origin of Absorption Spectra**, which we've defined earlier. This slide, titled Slide 6, delves into how these spectra arise.

* We start with an **Incident broadband light field**. "Broadband" means the light source emits over a continuous range of frequencies, or at least a range that is much wider than the absorption features we expect to see. This incident light has a spectral intensity denoted as $I_0(\nu)$, I naught of ν, where ν

is the frequency. This light then **passes through a gas cell** of a certain length, which we'll call Δz. This cell contains the atoms or molecules we want to study.

* Inside the gas cell, we have a population of atoms or molecules in their **lower-state, denoted** N_i. These atoms or molecules in state 'i' **can absorb photons** from the incident light field, but only if the photons have the correct energy, i.e., if their frequency corresponds to one of the allowed transition frequencies, or **eigenfrequencies,** ν_{ik}, for a transition from state 'i' to some upper state 'k'. This is the resonant absorption condition.

The ***Result*** *of this selective absorption is that when we look at the spectrum of the light* after* it has passed through the gas cell (the transmitted spectrum, $I(\nu)$), we will see **dips, or "dark lines,"** at those specific frequencies ν_{ik} where absorption occurred. The intensity of the transmitted light, $I(\nu)$, at these frequencies will be less than the incident intensity, $I_0(\nu)$. These dark lines against the brighter background of the incident continuum constitute the absorption spectrum.

* The **Absorption spectrum is then defined** based on this difference, as we'll see on the next page. This process is the basis of absorption spectroscopy, a cornerstone technique for identifying substances and determining their concentrations.

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Continuing from the previous slide, we now formally define the absorption spectrum, or more specifically, a quantity that characterizes it.

The **absorption coefficient,** $\alpha_{ik}(\nu)$, for a transition between states i and k at frequency ν, is defined as the fractional decrease in intensity per unit path length. Here it's given by the equation:

$$\alpha_{ik}(\nu) \equiv \frac{I_0(\nu) - I(\nu)}{\Delta z}$$

Let's break this down:

- $\alpha_{ik}(\nu)$: This is the absorption coefficient. It's a function of frequency, ν, because absorption is resonant. The subscripts 'i k' indicate it's for the specific transition from state 'i' to state 'k'. Its units are typically inverse length, like cm^{-1}.

- $I_0(\nu)$: This is the spectral intensity of the incident light at frequency ν before it enters the sample.

- $I(\nu)$: This is the spectral intensity of the transmitted light at frequency ν after passing through the sample of length Δz.

- Δz: This is the path length of the light through the sample.

The definition given on the slide, $\frac{I_0(\nu)-I(\nu)}{\Delta z}$, has units of (Intensity / length). This is not the standard definition of the absorption coefficient α, which is usually defined from Beer-Lambert law $\frac{dI}{dz} = -\alpha I$, leading to $I = I_0 \exp(-\alpha z)$. From this, $\alpha = \frac{1}{\Delta z} \ln\left(\frac{I_0}{I}\right)$.

The quantity $I_0 - I$ is the absorbed intensity. So $\frac{I_0-I}{\Delta z}$ is the absorbed intensity per unit length. This is related to α, especially for optically thin samples where $I_0 - I$ is small and $\frac{I_0-I}{I_0} \approx \alpha \Delta z$. If I_0 is factored in, $\frac{((I_0-I)/I_0)}{\Delta z}$ is closer to α for thin samples. Let's assume this is a simplified definition for the context, or related to power absorbed per unit volume if I_0 represents energy flux. For now, we will proceed with the slide's definition.

A crucial distinction is then made:

- If the **absorption is discrete**, meaning it leads to sharp lines, this implies that the upper state with energy E_k is a bound state. The atom or molecule transitions to a higher, but still bound, energy level.

- If the **absorption is a continuum**, meaning it's a broad, featureless absorption over a range of frequencies, this implies that the upper state E_k lies in an ionization or dissociation continuum. - For atoms, this means the absorbed photon has enough energy to completely remove an electron (photoionization), and any excess energy goes into the kinetic energy of the electron, which is not quantized. - For molecules, this could be photoionization, or it could be photodissociation, where the absorbed photon has enough energy to break a chemical bond, and the fragments fly apart with a continuous distribution of kinetic energies.

This distinction between discrete and continuous absorption is vital for interpreting the nature of the states involved.

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Slide 7:

Let's look at some **Illustrative Cases** that highlight these concepts.

1. **Atomic hydrogen:** The Lyman series in atomic hydrogen involves transitions from the $n = 1$ ground state to higher n states. As n approaches ∞, the energy levels converge to the ionization limit. Absorption of photons with energy greater than this limit (which is 13.6 eV, for hydrogen) results in photoionization. This leads to the **Lyman continuum, an area of continuous ultraviolet absorption above** 13.6 eV. So, if you shine UV light with photon energies greater than 13.6 eV onto hydrogen atoms, they will absorb this light continuously, producing photoelectrons with a range of kinetic energies.

2. **Molecular iodine (I_2)**: Iodine vapor is a classic example in spectroscopy. It has a very rich and complex absorption spectrum in the visible region. This

complexity arises because, in addition to electronic transitions, molecules also have vibrational and rotational energy levels. A single electronic transition can be accompanied by various changes in vibrational and rotational quantum numbers, leading to **billions of narrow rovibronic lines**. These are so dense that at lower resolution they might appear as broader bands. The fact that so many lines are visible at room temperature is **owing to the population of many initial rotational and vibrational energy states,** E_{i}, even within the ground electronic state, due to thermal energy.

3. **The Sun's photosphere and its cooler outer layers:** We've touched on this before. The hot, dense photosphere of the Sun emits a spectrum that is approximately like that of a black body – a continuous spectrum. As this light passes through the Sun's cooler, less dense outer atmosphere (the chromosphere), atoms and ions present in these layers absorb specific frequencies corresponding to their characteristic transitions. This results in the dark **Fraunhofer lines** superimposed on the continuous solar spectrum. We'll discuss these in more detail next.

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Let's focus on the example of **Fraunhofer Lines**, as presented on Slide 8.

* As mentioned, the **Sun's interior emits a nearly perfect black-body spectrum**. The effective temperature of the emitting surface, the photosphere, is approximately $T \approx 5800\,\mathrm{K}$. This hot region provides the continuous background of light.

* The Sun also has an **Outer gaseous atmosphere** (the chromosphere and corona) which is cooler and less dense than the photosphere. This atmosphere **contains various atoms and ions**, such as Sodium ($\mathrm{N\ a}$), Calcium ($\mathrm{C\ a}$), Iron ($\mathrm{F\ e}$), Hydrogen (H), and many others.

* As the continuous light from the photosphere passes through this cooler outer atmosphere, **those atoms absorb photons at their specific, characteristic eigenfrequencies,** ν_{ik}. This selective absorption removes light at these particular frequencies from the continuous spectrum. The result is the appearance of **narrow dark lines in the solar continuum** when we observe it from Earth. These are the Fraunhofer lines.

* A very **Famous example is the D1 and D2 sodium doublet at** 589.0 nm (actually 589.592 nm for D1 and 588.995 nm for D2). These are very prominent yellow lines in the solar spectrum, arising from the absorption by sodium atoms in the Sun's atmosphere. Their strength tells us about the abundance of sodium.

Fraunhofer lines were among the first spectroscopic observations that hinted at the chemical composition of stars, a revolutionary discovery at the time. Joseph von Fraunhofer meticulously cataloged hundreds of these lines in the early 19th century, even before their atomic origins were fully understood.

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This slide presents a visual representation of the **Solar Spectrum with Fraunhofer Lines**.

We are looking at a graph where the horizontal axis is **Wavelength in nanometers (nm)**, ranging from about 400 nm on the left (violet/blue) to 750 nm on the right (red). The spectrum itself is depicted as a continuous band of colors, like a rainbow, representing the black-body emission from the Sun's photosphere.

Superimposed on this continuous rainbow are several prominent **dark vertical lines**. These are the Fraunhofer lines, indicating wavelengths where light has been absorbed by elements in the Sun's cooler outer atmosphere. Let's point out some of the labeled lines:

Over in the violet/blue region, around 393.37 nm and 396.85 nm, are the **K and H lines of Calcium II** (singly ionized calcium). These are very strong.

Near 430.7 nm, there's the **G line**, which is a blend of lines from Iron I (neutral iron) and Calcium I (neutral calcium).

At 486.13 nm, in the blue-green region, is the **F line**, which corresponds to the **H-beta transition of Hydrogen**.

Prominently in the yellow region, at 589.0 nm and 589.59 nm (though only one position 589.59 nm is marked here for D2, implying the doublet), are the **D lines of Sodium I** (neutral sodium), specifically labeled D2 for the line at 589.59 nm.

In the red region, at 656.28 nm, is the **C line**, which corresponds to the **H-alpha transition of Hydrogen**.

There are many other labeled lines, such as those for Iron (Fe I) and Hydrogen delta (Hδ). The sheer number and varying intensities of these lines provide a wealth of information about the Sun's composition, temperature, and atmospheric conditions. Studying these lines is a cornerstone of astrophysics.

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Now that we've seen how absorption spectra arise and can be observed, we hit an important point on Slide 9: the **Need for a Quantitative Measure of "Absorption Strength"**.

* Simply looking at the **Qualitative line depth** in a spectrum – how "dark" or "deep" an absorption line appears – is often **insufficient for rigorous scientific comparison**. The apparent depth can be affected by the resolution of the spectrograph, by various line broadening mechanisms, and it doesn't easily allow us to compare the intrinsic strengths of different transitions, or

the same transition under different conditions of pressure or temperature. We need more robust, quantitative measures.

* To address this, a **Fundamental microscopic quantity is introduced: the absorption cross section, denoted** $\sigma_{ik}(\omega)$. We've mentioned this before. This $\sigma_{ik}(\omega)$, as a function of angular frequency ω, represents the intrinsic "effective area" that an atom or molecule in state 'i' presents to an incident photon of frequency ω for absorption to occur, leading to a transition to state 'k'. Its units are area (e.g., meters squared or centimeters squared). This is a key microscopic property of the transition.

* Correspondingly, there is a **Macroscopic measurable quantity: the absorption coefficient,** $\alpha_{ik}(\omega)$. This is what we typically determine from Beer's Law experiments. It's related to the absorption cross section but also depends on the concentration of absorbers. Its units are typically inverse length (e.g., per meter or per centimeter).

The goal is to connect these quantities and use them to rigorously describe absorption.

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Continuing from the previous point, this slide emphasizes a crucial link:

* These measures of absorption strength – the microscopic absorption cross section (σ) and the macroscopic absorption coefficient (α) – are **linked via the population density,** N_i, and the path length, Δz.

Specifically, the macroscopic absorption coefficient, α_{ik}, at a particular frequency is directly proportional to the microscopic absorption cross section, σ_{ik}, at that frequency, multiplied by the number density of absorbers in the initial state, N_i. That is:

$$\alpha_{ik} = N_\mathrm{i}\,\sigma_{ik}$$

This relationship is fundamental. σ_{ik} tells us about the intrinsic probability of a single atom/molecule absorbing. N_{i} tells us how many such absorbers there are per unit volume. Together, they determine α_{ik}, which describes how much light is attenuated per unit distance as it travels through the bulk material. The total absorption will then, of course, also depend on the total path length, Δz, through which the light interacts with the absorbing medium.

Understanding this connection allows us to move between the microscopic world of individual atomic/molecular properties and the macroscopic world of measurable optical phenomena.

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Slide 10 provides an intuitive, albeit classical, **Geometric Picture for the Absorption Cross Section**.

* First, we are asked to **Imagine photons as classical particles moving in a parallel beam**, like tiny bullets.

* Then, we imagine that **Each atom presents an effective circular "target" of radius** r_{ik} for a specific transition i to k. The absorption cross section, σ_{ik}, is then simply the area of this target:

$$\sigma_{ik} = \pi(r_{ik})^2$$

The units are, of course, area, for example, meters squared, as indicated.

* The idea is that a **Photon hitting this area** σ_{ik} has a probability approximately equal to 1 to be absorbed by the atom, causing it to undergo the transition from the initial quantum state, $|i\rangle$, to the final quantum state, $|k\rangle$. Photons missing this target area pass by unabsorbed.

* Crucially, this is a simplified picture. The "radius" r_{ik} is not a fixed physical dimension of the atom. In reality, the **Cross section depends strongly on the frequency,** ω, of the incident photon. It is **sharply peaked at the resonant**

frequency, ω_{ik}, corresponding to the energy difference $E_k - E_i$. Away from resonance, the effective target area shrinks dramatically. So, $\sigma_{ik}(\omega)$ is really a function that describes how the absorption probability varies with frequency.

While this classical geometric analogy helps build intuition, the true nature of the absorption cross section is rooted in quantum mechanics and the interaction of the electromagnetic field with the atomic or molecular dipole moment. However, thinking of it as an "effective area" is a very useful conceptual tool.

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Now we move into a more quantitative derivation. Slide 11 begins the process of **Deriving the Absorbed Power Expression**, which is labeled as Equation 2.58 (likely from a reference textbook). This will be a **Step-by-step calculation for an infinitesimal slice** of the absorbing medium.

1. First, we define the **Spectral intensity of the incident beam as** $I_0(\omega)$, or $I_0(\omega)$. The units given are Watts per meter squared per radian per second, times seconds. This is Watt meter to the minus two, radian to the minus one, second to the minus one, second. This unit is a bit unusual. Spectral intensity (or radiance in some contexts) is typically power per unit area, per unit solid angle, per unit frequency interval. If ω is angular frequency (radians per second), then "per radian per second" would be per unit angular frequency. The final "s" might be a typo or refer to a specific integration time. Let's assume $I_0(\omega)$ is power per unit area per unit angular frequency interval: [Watts meter to the minus 2 (radian/second) to the minus 1].

2. Next, we define the **Photon spectral flux density,** Φ. This is the number of photons per unit area, per unit time, per unit angular frequency interval. It's obtained by taking the spectral intensity $I_0(\omega)$ and dividing it by the energy of a single photon at that angular frequency, which is $\hbar\,\omega$:

$$\Phi = \frac{I_0(\omega)}{\hbar\,\omega}$$

The units would be [photons meter to the minus 2 second to the minus 1 (radian/second) to the minus 1].

3. Now, consider the **Number of photons crossing an area** A in an infinitesimal time dt and within an infinitesimal angular frequency range $d\omega$. This quantity, let's call it dN_γ (for photons), would be given by the photon spectral flux density times area, times time interval, times angular frequency interval. The formula will be on the next slide.

This sets up the initial conditions for calculating how many photons are absorbed.

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Continuing our step-by-step derivation:

The number of incident photons, dN_γ, crossing area A in time dt and frequency range $d\omega$ is given by:

$$dN_\gamma = \Phi \cdot A \cdot dt \cdot d\omega$$

This is consistent with our definition of Φ as photon spectral flux density.

4. Next, we determine the **Number of absorbers available in an infinitesimal slice of thickness** Δz. If N_i is the number density of absorbers in the initial state 'i' (number per unit volume), and the slice has a cross-sectional area A and thickness Δz, then its volume is $A \cdot \Delta z$. So, the number of absorbers in this slice is:

$$N_\mathrm{i} \cdot A \cdot \Delta z$$

5. Now, we need the **Net transition probability per absorber**. Let's call this P_abs. The slide gives it as:

$$P_{\text{abs}} = \sigma_{ik}(\omega) \cdot \Phi \cdot dt$$

Here, $\sigma_{ik}(\omega)$ is the absorption cross section. If Φ is the photon spectral flux density as defined on the previous slide, then Φ has units of [photons / (area × time × angular_frequency_interval)]. Multiplying σ (area) by Φ gives [photons / (time × angular_frequency_interval)], which is a rate of photon incidence per unit frequency interval through the cross-sectional area. Multiplying by dt gives [photons / angular_frequency_interval]. This is the number of photons incident on one atomic cross-section within the bandwidth $d\omega$ (if $d\omega$ is implicitly part of Φ or applied later) during time dt. For this to be a *probability*, Φ here should perhaps be the photon flux (photons / area / time) and the result would be probability per unit frequency interval. Let's assume that P_{abs} here represents the probability that a single absorber, when exposed to the photon spectral flux density Φ within a certain bandwidth $d\omega$ (which might be implicit in Φ or P_{abs} itself), makes a transition in time dt. A more standard approach: rate of absorption per atom = $\sigma_{ik}(\omega)$ × PhotonFlux$_{\omega}$. Then probability in dt is this rate × dt. The slide's formulation appears to be a slight simplification. Let's follow its logic.

6. With this, the total **Photons removed (absorbed) from the beam** in this slice, dN_{abs}, is the number of absorbers times the probability of absorption per absorber:

$$dN_{\text{abs}} = (N_{\text{i}} \cdot A \cdot \Delta z) \cdot P_{\text{abs}}$$

Substituting P_{abs} from step 5:

$$dN_{\text{abs}} = N_{\text{i}} \cdot A \cdot \Delta z \cdot \sigma_{ik}(\omega) \cdot \Phi \cdot dt$$

7. The **Energy removed from the beam in time** dt, which we'll call dW_{ik}, is the number of photons absorbed times the energy per photon ($\hbar\omega$):

$$dW_{ik} = dN_{\text{abs}} \cdot (\hbar\omega)$$

8. Finally, to get the differential power absorbed, we **Divide** dW_{ik} by dt. The resulting expression will be on the next page.

This derivation, despite some potential subtleties in the definition of P_{abs}, aims to link the microscopic cross section to macroscopic power absorption.

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Following from the previous steps, the expression for the absorbed power within the angular frequency interval $\mathrm{d}\omega$ is presented here. Note, the percent sign

in front of

is likely a typo and should be a lowercase

for differential. So, let's read it as:

$$\mathrm{d}P_{ik}(\omega)\,\mathrm{d}\omega = I_0(\omega)\left[N_{\mathrm{i}} - \frac{g_{\mathrm{i}}}{g_{\mathrm{k}}}N_{\mathrm{k}}\right]\sigma_{ik}(\omega)\,A\Delta z\,\mathrm{d}\omega$$

This equation represents the power absorbed from the incident light beam as it passes through the infinitesimal slice of material. Let's dissect each term:

* $\mathrm{d}P_{ik}(\omega)\,\mathrm{d}\omega$: This is the infinitesimal amount of power absorbed from the light field within the angular frequency range $\mathrm{d}\omega$, due to transitions from state i to state k.

* $I_0(\omega)$: This is the spectral intensity of the incident light (power per unit area per unit angular frequency).

$\left[N_{\mathrm{i}} - \frac{g_{\mathrm{i}}}{g_{\mathrm{k}}}N_{\mathrm{k}}\right]$: This is a critical term. It represents the effective population difference* between the lower state 'i' and the upper state 'k'. * N_{i} is the population density of atoms in the lower state, which contribute to absorption. * N_{k} is the population density of atoms in the upper state. These atoms can be stimulated by the incident photons to emit a photon, a process called stimulated emission. Stimulated emission adds photons to the beam that are identical to the incident photons, so it effectively counteracts absorption. * g_i and g_k are the statistical weights (or degeneracies) of the lower and upper states, respectively. These factors account for the fact that energy levels can consist of multiple degenerate sub-levels. The ratio $\frac{g_\mathrm{i}}{g_\mathrm{k}}$ correctly weights the contribution of stimulated emission relative to absorption, as dictated by detailed balance and Einstein's relations. If this term $\left[N_\mathrm{i} - \frac{g_\mathrm{i}}{g_\mathrm{k}} N_\mathrm{k}\right]$ is positive, net absorption occurs. If it's negative, net amplification occurs (as in a laser).

* $\sigma_{ik}(\omega)$: This is the absorption cross section for the transition at angular frequency ω.

* $A\Delta z$: This is the volume of the infinitesimal slice (Area times thickness).

* $\mathrm{d}\omega$: This is the infinitesimal angular frequency interval.

The slide correctly notes that the **Statistical weights** g_i, g_k (degeneracy) are included to allow for the stimulated emission correction. Without this correction, we would overestimate the net absorption, especially if the population N_k of the upper state is significant. This equation forms the basis for understanding light attenuation or amplification in a medium.

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Slide 12: Integrating Over the Line Profile and its Link to the Einstein B_{ik}

* First, we **Define the absorption coefficient, alpha sub i k of omega**. Based on the expression for absorbed power from the previous slide, the absorption coefficient (which describes attenuation per unit length) is:

$$\alpha_{ik}(\omega) = \sigma_{ik}(\omega) \left[N_\mathrm{i} - \frac{g_\mathrm{i}}{g_\mathrm{k}} N_\mathrm{k}\right]$$

Recall from Beer-Lambert law, $\frac{dI}{dz} = -\alpha I$. The power absorbed in a volume $dV = A\,dz$ is $dP = \alpha I\,dV$. Comparing with the previous slide's equation, $dP = I_0(\omega)\left[N_\mathrm{i} - \frac{g_\mathrm{i}}{g_\mathrm{k}}N_\mathrm{k}\right]\sigma_{ik}(\omega)A\,dz\,d\omega$, we see this definition of alpha is consistent. It has units of inverse length (e.g., m^{-1} or cm^{-1}).

* Next, we consider the total **Absorbed power in a finite volume delta V equals A times delta zed**. To get the total power absorbed by atoms undergoing the i to k transition, we need to integrate the spectral absorption over the entire line profile. The slide shows this as:

$$P_{ik} = I_0\,\Delta V \int_{-\infty}^{+\infty} \alpha_{ik}\,(\omega)\,d\omega$$

Here, P_{ik} is the total power absorbed from the beam integrated over all frequencies of the transition. A couple of points about this equation:

- I_0 is pulled out of the integral. This implies that the incident spectral intensity I_0 is assumed to be constant over the frequency range where $\alpha_{ik}(\omega)$ is significant, or I_0 represents its value at the line center, ω_{ik}. For a broadband source, this is often a good approximation. - The integral $\int \alpha_{ik}(\omega)\,d\omega$ is the integrated absorption coefficient. It represents the total strength of the absorption line. - The limits of integration from minus infinity to plus infinity are formal; in practice, $\alpha_{ik}(\omega)$ is only non-zero in a narrow region around the resonant frequency.

This expression for total absorbed power, based on macroscopic quantities, will then be compared to an expression based on the microscopic Einstein B_{ik} coefficient.

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Now we **Compare** the expression for absorbed power we just derived with the one based on the **Einstein rate expression**.

The Einstein rate expression for the power absorbed is given on the slide as:

$$\frac{h\nu}{c}\, I_0\, B_{ik}\left(N_{\mathrm{i}} - \frac{g_{\mathrm{i}}N_{\mathrm{k}}}{g_{\mathrm{k}}}\right)\Delta V$$

Let's analyze this. The rate of stimulated absorption transitions per unit volume is $\left(N_{\mathrm{i}} - \frac{g_{\mathrm{i}}}{g_{\mathrm{k}}}N_{\mathrm{k}}\right)B_{ik}^{(\nu)}\rho_\nu(\nu_{ik})$, where $B_{ik}^{(\nu)}$ is the Einstein B coefficient for frequency ν and ρ_ν is the spectral energy density per unit frequency. The power absorbed in volume ΔV is this rate times $h\nu_{ik}$ times ΔV.

If we relate energy density ρ_ν to intensity I_0 (intensity per unit frequency interval from a beam) by $\rho_\nu = \frac{I_0}{c}$ (this is for a beam, for isotropic radiation it would be $\frac{4\pi I_0}{c}$), then the power absorbed becomes:

$$P_{ik} = \left(N_{\mathrm{i}} - \frac{g_{\mathrm{i}}}{g_{\mathrm{k}}}N_{\mathrm{k}}\right)B_{ik}^{(\nu)}\left(\frac{I_0}{c}\right)h\nu_{ik}\,\Delta V$$

This matches the form on the slide, assuming B_{ik} is $B_{ik}^{(\nu)}$ and I_0 is intensity per unit frequency.

By equating this Einstein-based expression for absorbed power with the one from the previous slide

$$P_{ik} = I_0\,\Delta V \int \alpha_{ik}(\nu)\,d\nu$$

(switching to ν for consistency with $h\nu$), and noting

$$\alpha_{ik}(\nu) = \sigma_{ik}(\nu)\left(N_{\mathrm{i}} - \frac{g_{\mathrm{i}}}{g_{\mathrm{k}}}N_{\mathrm{k}}\right),$$

we can isolate the microscopic parameter B_{ik}.

The slide shows (with

being a typo for B_{ik} and assuming $h\nu$ should be $\hbar\omega_{ik}$ to match the integral over $d\omega$):

$$B_{ik} = \frac{c}{\hbar\omega_{ik}} \int_{-\infty}^{+\infty} \sigma_{ik}\,(\omega)\, d\omega$$

This relates the Einstein B coefficient (here, $B_{ik}^{(\omega)}$ defined for angular frequency energy density ρ_ω) to the integrated absorption cross section.

Let's verify:

$$P_{ik} = N_{\mathrm{i}}^{eff}\, B_{ik}^{(\omega)}\, \rho_\omega(\omega_{ik})\, \hbar\omega_{ik}\, \Delta V$$

Using $\rho_\omega = \frac{I_0^{(\omega)}}{c}$, where $I_0^{(\omega)}$ is intensity per unit angular frequency,

$$P_{ik} = N_{\mathrm{i}}^{eff}\, B_{ik}^{(\omega)} \left(\frac{I_0^{(\omega)}}{c}\right) \hbar\omega_{ik}\, \Delta V$$

Also,

$$P_{ik} = I_0^{(\omega)}\, \Delta V \int \sigma_{ik}(\omega)\, N_{\mathrm{i}}^{eff}\, d\omega$$

Equating these:

$$B_{ik}^{(\omega)} \frac{\hbar\omega_{ik}}{c} = \int \sigma_{ik}(\omega)\, d\omega$$

So,

$$B_{ik}^{(\omega)} = \frac{c}{\hbar\omega_{ik}} \int \sigma_{ik}(\omega)\, d\omega$$

This matches the slide if B_{ik} is $B_{ik}^{(\omega)}$ and $h\nu$ is interpreted as $\hbar\omega_{ik}$.

The **Integral over sigma sub i k** is, as noted, sometimes called the "cross-sectional area under the line" or, more commonly, the **integrated cross section**. It's a fundamental measure of the total interaction strength for that transition, irrespective of broadening effects.

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We now advance to Slide 13, where we consider a more realistic scenario by **Including Thermal (Boltzmann) Populations**. In many situations, especially in gases at or near thermal equilibrium, the populations of the energy levels are governed by the Boltzmann distribution.

* **At thermal equilibrium temperature** T Kelvin:

The population of an energy level 'i', denoted N_i, is given by:

$$N_\mathrm{i} = \frac{N\, g_\mathrm{i}}{Z}\, e^{-\frac{E_\mathrm{i}}{k_\mathrm{B} T}}.$$

Let's break this down: * N is the total number density of atoms or molecules. * g_i is the degeneracy of state 'i'. * E_i is the energy of state 'i'. * k_B is the Boltzmann constant (one point three eight times ten to the minus twenty-three Joules per Kelvin, rendered as 1.38×10^{-23} Joules per Kelvin). * T is the absolute temperature in Kelvin. * Z is the **partition function**, which is a sum over all possible states 'j': $Z = \sum_j g_\mathrm{j}\, e^{-\frac{E_\mathrm{j}}{k_\mathrm{B} T}}$ The partition function acts as a normalization factor, ensuring that the sum of populations N_j over all states equals the total number density N. The Boltzmann factor, $\exp(-E_\mathrm{i}/k_\mathrm{B}T)$, shows that higher energy states are exponentially less populated at a given temperature.

* **Substituting these Boltzmann population expressions for** N_i and N_k into our previous power formula gives:

Recall the absorbed power

$$P_{ik} = I_0 \Delta V \int \alpha_{ik}(\omega)\, d\omega = I_0 \Delta V \int \sigma_{ik}(\omega) \left[N_\mathrm{i} - \frac{g_\mathrm{i}}{g_\mathrm{k}} N_\mathrm{k}\right] d\omega.$$

Substituting for N_i and N_k:

$$P_{ik} = I_0 \Delta V \left[\frac{N}{Z}\left(g_\mathrm{i}\, e^{-\frac{E_\mathrm{i}}{k_\mathrm{B} T}} - g_\mathrm{k}\, e^{-\frac{E_\mathrm{k}}{k_\mathrm{B} T}}\right)\right] \int \sigma_{ik}(\omega)\, d\omega.$$

This explicitly shows how the absorbed power depends on temperature T through the Boltzmann populations in N_{i} and N_{k}, and through the partition function Z.

* Now, a common approximation is considered: the **Low-frequency (Far-Infrared or FIR) limit**. This applies when the energy difference between the states, $E_{\mathrm{k}} - E_{\mathrm{i}}$ (which is $\hbar\omega_{ik}$), is much less than the thermal energy, $k_{\mathrm{B}}T$: $E_{\mathrm{k}} - E_{\mathrm{i}} \ll k_{\mathrm{B}}T$.

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Continuing with the low-frequency (FIR) limit:

When $(E_{\mathrm{k}} - E_{\mathrm{i}}) \ll k_{\mathrm{B}}T$, we can approximate the exponential term for the upper state population. The energy of the upper state is $E_{\mathrm{k}} = E_{\mathrm{i}} + \hbar\omega_{ik}$.

So, $\exp\left(-\frac{E_{\mathrm{k}}}{k_{\mathrm{B}}T}\right) = \exp\left(-\frac{E_{\mathrm{i}}+\hbar\omega_{ik}}{k_{\mathrm{B}}T}\right) = \exp\left(-\frac{E_{\mathrm{i}}}{k_{\mathrm{B}}T}\right) \cdot \exp\left(-\frac{\hbar\omega_{ik}}{k_{\mathrm{B}}T}\right)$.

Since $\frac{\hbar\omega_{ik}}{k_{\mathrm{B}}T}$ is small (let $x = \frac{\hbar\omega_{ik}}{k_{\mathrm{B}}T}$), we can use the Taylor expansion $\exp(-x) \approx 1 - x$ for small x.

Therefore, $\exp\left(-\frac{E_{\mathrm{k}}}{k_{\mathrm{B}}T}\right)$ is approximately equal to $\exp\left(-\frac{E_{\mathrm{i}}}{k_{\mathrm{B}}T}\right)$ times the quantity $\left(1 - \frac{E_{\mathrm{k}}-E_{\mathrm{i}}}{k_{\mathrm{B}}T}\right)$.

Substituting this into the population difference term $\left[g_{\mathrm{i}}\exp\left(-\frac{E_{\mathrm{i}}}{k_{\mathrm{B}}T}\right) - g_{\mathrm{k}}\exp\left(-\frac{E_{\mathrm{k}}}{k_{\mathrm{B}}T}\right)\right]$ from the previous slide: It becomes approximately

$$\exp\left(-\frac{E_{\mathrm{i}}}{k_{\mathrm{B}}T}\right) \cdot \left[g_{\mathrm{i}} - g_{\mathrm{k}}\left(1 - \frac{E_{\mathrm{k}} - E_{\mathrm{i}}}{k_{\mathrm{B}}T}\right)\right].$$

If we further assume $g_{\mathrm{i}} = g_{\mathrm{k}} = g$ for simplicity, this becomes:

$$g \cdot \exp\left(-\frac{E_{\mathrm{i}}}{k_{\mathrm{B}}T}\right) \cdot \left[1 - \left(1 - \frac{E_{\mathrm{k}} - E_{\mathrm{i}}}{k_{\mathrm{B}}T}\right)\right] = g \cdot \exp\left(-\frac{E_{\mathrm{i}}}{k_{\mathrm{B}}T}\right) \cdot \frac{E_{\mathrm{k}} - E_{\mathrm{i}}}{k_{\mathrm{B}}T}.$$

This population difference is proportional to $\frac{1}{T}$.

The slide presents a final expression for P_{ik} in this limit, which seems to be further approximated for the line shape (using $\sigma_{ik}(\omega_0)$ which is peak cross section): P_{ik} is approximately equal to $I_0\,\sigma_{ik}(\omega_0)\left(\frac{Ng_\mathrm{i}}{Zk_\mathrm{B}T}\right)\Delta V$.

For this expression to have units of power, it needs an additional factor of $(E_\mathrm{k}-E_\mathrm{i})$ or $\hbar\omega_0$ or a frequency bandwidth. For instance, if the term $(E_\mathrm{k}-E_\mathrm{i})$ that arose from the expansion was $\hbar\omega_0$, then

$$P_{ik} \approx I_0\,\sigma_{ik}(\omega_0)\,\frac{Ng_\mathrm{i}\exp\left(-\frac{E_\mathrm{i}}{k_\mathrm{B}T}\right)}{Z}\,\frac{\hbar\omega_0}{k_\mathrm{B}T}\,\Delta V\,\Delta\omega_\mathrm{eff}$$

where $\Delta\omega_\mathrm{eff}$ is an effective bandwidth.

The key result here is the $\frac{1}{T}$ dependence.

* The important takeaway here is that this analysis **Demonstrates that Far-Infrared (FIR) absorption strength is proportional to** $\frac{1}{T}$ (one over T). This is **intuitive because** in this regime, the photon energy $\hbar\omega_{ik}$ is small, comparable to or less than $k_\mathrm{B}T$. As temperature increases, thermal energy $k_\mathrm{B}T$ becomes more effective at populating the upper state k via collisions, thus reducing the population difference $N_\mathrm{i}-\left(\frac{g_\mathrm{i}}{g_\mathrm{k}}\right)N_\mathrm{k}$. This, in turn, reduces the net absorption. The lower photon energy has to "compete" more strongly with thermal excitation at higher temperatures.

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Slide 14:

discusses a **Practical "Figure-of-Merit" for Detecting Absorption** and strategies to enhance the signal.

* The **Signal size** in an absorption experiment is generally proportional to the product of three factors: $N_\mathrm{i} \times \sigma_{ik} \times \Delta_\mathrm{z}$.

* N_i: The number density of absorbers in the initial state. More absorbers mean more potential absorption. * σ_{ik}: The absorption cross section. A larger cross section means a higher probability of absorption per atom/molecule. * Δ_z: The path length of the light through the sample. A longer path means more interaction opportunities.

Maximizing this product $N_\mathrm{i} \times \sigma_{ik} \times \Delta_\mathrm{z}$ is key to achieving a strong absorption signal.

* So, **To increase detection sensitivity** (i.e., to make it easier to detect weak absorption), we can try to manipulate these factors:

1. Increase number density N (which generally increases N_i). For gases, this often means **raising the pressure**. However, there's a caveat: **beware of collisional broadening** (also known as pressure broadening). While increasing pressure increases N, it also increases the collision rate between molecules. These collisions perturb the energy levels and shorten the effective lifetime of quantum states, leading to broader spectral lines. A broader line might have a lower peak absorption cross section, $\sigma_{ik}(\omega_0)$, even if the integrated cross section S_{ik} remains the same or increases. So, there's often an optimal pressure.

2. Prolong path length Δ_z. This is a very common strategy. * One can use a **long cell**. * More sophisticated are **multi-pass cells** (like White cells or Herriott cells) where mirrors reflect the beam back and forth through the sample many times, achieving effective path lengths of meters or even kilometers in a compact setup. * Advanced techniques involve placing the sample inside an **optical cavity** (e.g., Cavity Ring-Down Spectroscopy - CRDS, or Cavity Enhanced Absorption Spectroscopy - CEAS), which can result in extremely long effective path lengths.

3. Select transitions with large σ_{ik}. This involves choosing molecular transitions that are intrinsically strong. * Typically, this means looking for transitions originating from low E_i states (i.e., the ground state or low-lying excited states), because these states will have higher populations N_i according to the Boltzmann distribution. * It also means choosing transitions with a **high oscillator strength,** f_{ik}, as oscillator strength is directly related to the intrinsic strength of the transition and thus to σ_{ik}.

These are practical considerations for designing sensitive absorption spectroscopy experiments.

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This slide reiterates a key point regarding thermally populated samples:

* **For thermally populated gases: observe transitions originating from the ground state or few first excited states.**

This is a direct consequence of the Boltzmann distribution, $N_\mathrm{i} \propto \exp\left(-\frac{E_\mathrm{i}}{k_\mathrm{B}T}\right)$. At typical laboratory temperatures (e.g., room temperature, around $300\,\mathrm{K}$), the thermal energy $k_\mathrm{B}T$ is about 0.026 electron-Volts or roughly 200 inverse centimeters.

* Electronic ground states are, by definition, the most populated. * Excited electronic states are usually many $k_\mathrm{B}T$ units above the ground state, so their thermal populations are negligible. * For molecules, low-lying rotational and vibrational states within the ground electronic state can be significantly populated at room temperature.

However, **higher** E_i levels (higher vibrational states, or certainly higher electronic states) **are sparsely populated**. Consequently, absorption lines originating from these high-energy initial states will be very weak or undetectable in a thermal equilibrium sample.

This is why most absorption spectroscopy on thermal samples focuses on transitions from the ground state or very low-lying excited states.

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Slide 15

introduces **Non-Thermal Population Strategies**. What if we want to study transitions that originate from states that are not significantly populated at thermal equilibrium? We need ways to prepare non-thermal populations.

One powerful technique is ***Optical pumping****. This involves using an* ***intense, narrowband laser to drive population from a lower state (e.g., the ground state,*** $|g\rangle$) to a specific excited state, $|e\rangle$. By continuously shining this "pump" laser, tuned to the g-to-e transition, we can create a significant population in the excited state $|e\rangle$, far exceeding its thermal population. We can then perform spectroscopy from* this artificially populated state $|e\rangle$ using a second "probe" laser.

* Another method is **Electron impact**. This is common in **discharge tubes or plasmas**. In a discharge, free electrons are accelerated by an electric field and gain kinetic energy. When these energetic electrons collide with atoms or molecules, they can transfer energy, exciting the atoms/molecules to various **high-lying states**. This process is not governed by thermal equilibrium, and can populate states that would otherwise be empty.

* The **Result** of using such non-thermal population strategies is that they **allow the study of absorption lines originating from initial states** E_i that are otherwise unpopulated (or very sparsely populated) at room temperature. This opens up the possibility of exploring a much wider range of energy levels and transitions within atoms and molecules. For example, one could study absorption from an excited electronic state to even higher electronic states.

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This slide provides a **Schematic Energy Levels diagram for Pump-Probe Spectroscopy**, which often utilizes optical pumping to create non-thermal populations.

We see three energy levels depicted: * E_g: The ground state, labeled with the ket $|g\rangle$. * E_e: An intermediate excited state, labeled with the ket $|e\rangle$. * E_f: A higher excited state, labeled with the ket $|f\rangle$.

The process unfolds as follows: 1. **Pump**: An intense "pump" laser, with photon energy $h\nu_{\text{pump}}$ (represented by the upward red arrow), excites the system from the ground state E_g to the intermediate excited state E_e. This creates a population in state $|e\rangle$. 2. **Probe Absorption**: A second "probe" laser, with photon energy $h\nu_{\text{probe}}$ (represented by the upward blue arrow), can then induce transitions from the populated state E_e to a still higher state E_f. By monitoring the absorption of this probe laser, we can study the properties of state E_e or the dynamics of its population.

The diagram also shows various **Decay paths** from state E_e, which are crucial for understanding the dynamics: * **Radiative Decay (e.g., Fluorescence)**: State $|e\rangle$ can decay back to the ground state E_g (or other lower states) by emitting a photon, $h\nu_{\text{decay}}$ (represented by the downward orange arrow). * **Non-Radiative Decay**: State $|e\rangle$ can also lose energy through non-radiative processes, such as collisions, transferring its energy into heat. This is indicated by the dotted purple arrow labeled "Non-Radiative Decay" also leading to depopulation of $|e\rangle$. * The diagram also has a label "Probe Absorption" next to a dotted purple arrow that seems to indicate a decay pathway from E_e towards E_g, possibly also non-radiative or part of the overall relaxation dynamics that repopulate E_g.

Pump-probe spectroscopy is a powerful time-resolved technique. By varying the time delay between the pump and probe pulses, one can monitor how the population of state $|e\rangle$ evolves over time due to these decay processes, or how the ground state $|g\rangle$ recovers. This allows for the measurement of lifetimes, relaxation rates, and other dynamic processes.

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Now we shift our focus to emission processes, specifically **Fluorescence**, which is defined on Slide 16 as **Spontaneous Emission from Excited States**.

* Consider an atom or molecule in an **Excited state,** E_k. This state is not stable indefinitely; the system will eventually relax to a lower energy state. There are several ways it can do this:

1. **Spontaneous radiative decay (fluorescence):** The excited atom/molecule can spontaneously emit a photon and transition to a lower energy state. This emission of light is what we call fluorescence (or phosphorescence, if it involves a change in spin multiplicity and has a longer lifetime). This process does not require any external radiation field to trigger it; it's a fundamental quantum process.

2. **Stimulated emission (if a strong field is present):** If the excited atom/molecule is bathed in a radiation field of the appropriate frequency (i.e., resonant with the $E_\mathrm{k} \rightarrow E_\mathrm{i}$ transition), it can be stimulated to emit a photon. This photon will be identical to the stimulating photons. This process is crucial for lasers, but it requires an existing radiation field.

3. **Non-radiative collisions:** The excited atom/molecule can lose its energy through collisions with other atoms or molecules, converting its excitation energy into kinetic energy (heat) of the collision partners. This is often referred to as quenching.

In fluorescence spectroscopy, we are primarily interested in the first process: spontaneous radiative decay. The relative importance of these three pathways depends on the specific system and its environment (e.g., pressure, temperature, presence of a radiation field).

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Let's consider some characteristics of fluorescence:

* **If the molecular ensemble is randomly oriented, the spontaneous emission intensity is isotropic.** This means that the fluorescence is emitted equally in all directions. This is typically the case for gases or solutions where the molecules have no preferred orientation. However, if the molecules are aligned (e.g., in a crystal or by using polarized excitation light), the emission can be anisotropic (polarized).

* The **Observed fluorescence spectrum mirrors all allowed transitions from the populated excited state(s)** E_k down to various lower energy states E_i. The intensity of each emission line in this spectrum is **weighted by their respective transition probabilities** (Einstein A coefficients, A_{ki}) **and by the populations of the specific excited states** E_k from which the transitions originate. So, if you excite a molecule to a particular E_k, it might be able to fluoresce to several different lower-lying E_i levels. The resulting spectrum will show lines corresponding to each of these allowed downward transitions, and their relative intensities will depend on how probable each transition is and how many molecules were in that initial E_k state.

Fluorescence spectroscopy is a very sensitive technique because you are typically detecting emitted photons against a dark background, as opposed to absorption spectroscopy where you look for small decreases in a bright signal.

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Slide 17 discusses the distinction between **Discrete vs. Continuous Fluorescence**, which depends on the nature of the lower state involved in the emission.

1. If the fluorescence transition occurs from a bound excited state to a **Bound lower state** E_{i}, it **produces discrete line fluorescence**. Just like in absorption, if both the initial (upper) and final (lower) states are quantized and bound, the energy difference is fixed, leading to the emission of photons at specific, sharp frequencies. This results in a spectrum of discrete emission lines.

2. However, if the fluorescence transition occurs from a bound excited state to a **Repulsive (dissociative) lower state** E_{i}, or to a continuum of states above a dissociation or ionization limit, it **produces broad continuum fluorescence**.

* A repulsive state is one where there is no potential energy minimum to support bound vibrational levels; as soon as the molecule enters such a state, it flies apart.

* If the transition terminates above the dissociation limit of a bound lower state potential, the molecule also dissociates. In both cases, the energy of the final state is not quantized but can take on a continuous range of values (corresponding to the kinetic energy of the fragments). This leads to the emission of photons over a continuous range of frequencies, resulting in a broad, featureless emission band.

* An interesting point for continuum fluorescence, especially in molecules: The **Transition probability versus internuclear distance** R determines how vibrational wavefunction nodes imprint modulation on the continuum. According to the Franck-Condon principle, electronic transitions are "vertical" on a potential energy diagram. The intensity of the emission at a particular frequency in the continuum is related to the square of the overlap integral between the vibrational wavefunction of the bound upper state and the (continuum) wavefunction of the repulsive lower state. If the upper state vibrational wavefunction has nodes (points where its amplitude is zero), this

can lead to minima or characteristic oscillatory structures in the intensity profile of the continuous fluorescence spectrum. This is often called the "reflection principle" because the continuum spectrum can appear to reflect the shape of the upper state vibrational wavefunction.

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This diagram beautifully illustrates the concept of **Bound Upper State to Repulsive Lower State Fluorescence**.

We are looking at a potential energy diagram where the vertical axis is **Potential Energy,** $V(R)$, and the horizontal axis is **Internuclear Distance,** R (for a diatomic molecule).

* The **Upper electronic state,** E_k (Bound), is represented by the blue curve, which shows a typical potential energy well. This well can support discrete vibrational energy levels, a few of which are indicated by horizontal lines within the well. The minimum of this well is at an equilibrium internuclear distance R_e.

* The **Lower electronic state,** E_i (Repulsive), is represented by the red curve. This curve is purely repulsive; it continuously decreases in energy as R increases, meaning that if the molecule finds itself on this potential energy surface, the two atoms will repel each other and the molecule will dissociate.

Now, imagine the molecule is initially excited to one of the vibrational levels in the upper bound state E_k. From there, it can undergo fluorescence by transitioning down to the lower repulsive state E_i. These transitions are shown by the vertical green arrows, originating from different points along the upper potential well (representing the classical turning points of a particular vibrational level, or more accurately, regions where the vibrational wavefunction has significant amplitude).

Because the lower state E_{i} is repulsive, for any R value where the transition terminates, the molecule flies apart, and the energy released as fluorescence (the length of the green arrow) plus the kinetic energy of the fragments equals the energy of the upper vibrational level relative to the separated atoms limit of the lower state. Since the kinetic energy of the fragments can be continuous, the emitted photon energy can also be continuous.

This results in **Fluorescence (Continuum)**, a broad emission spectrum, as indicated. The intensity distribution of this continuum will reflect the projection of the upper state vibrational wavefunction onto the lower repulsive curve, according to the Franck-Condon principle.

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Slide 18

Slide 18 presents a **Case Study: the NaK Molecule (Sodium-Potassium) and a transition from a** 3Π state to a 3Σ state (triplet Π to triplet Σ electronic states). This is an example of molecular fluorescence that can exhibit both discrete and continuous features.

The **Upper state** involved is a specific **bound vibrational level within the** 3Π electronic state, which is populated by excitation with an **Argon-ion laser**. Argon-ion lasers have several discrete emission lines, and one of these can be chosen to selectively pump the NaK molecules to a particular rovibrational level of the 3Π state.

The **Lower electronic state is the** 3Σ state. This state is described as having a **shallow van der Waals well**, with its **dissociation limit,** D_0, lying just above some of its lower vibrational energy levels E_{i}. A van der Waals well is typically much shallower and has a larger equilibrium internuclear distance than a normal chemical bond.

Now, depending on the energy of the emitting vibrational level in the upper 3Π state relative to the features of the lower 3Σ state:

If the transition from the upper state terminates on the **High-energy part of the lower** 3Σ potential, specifically to energies E_k that are above the dissociation limit D_0 of this lower state, then this results in **continuum fluorescence**. The molecule dissociates upon emission. (Here, E_k seems to refer to the energy of the emitted photon relative to the bottom of the lower state, or perhaps E_k is the energy of the upper level, and the transition energy is such that it lands above D_0).

Conversely, if the transition terminates on the **Low-energy part of the lower** 3Σ potential, into one of the bound vibrational levels within its shallow well (i.e., the transition energy results in a final state energy E_k that is less than D_0), then this results in **discrete bound-bound lines**.

For the continuum part of the fluorescence, the **Continuum intensity is modulated by the overlap integral** between the vibrational wavefunction of the initial (upper 3Π) state and the continuum wavefunctions of the final (lower 3Σ) dissociative state. This is the Franck-Condon effect we discussed.

This example beautifully illustrates how a single excited state can lead to both discrete and continuous emission features, depending on the nature of the lower potential energy surface it transitions to.

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This slide provides the mathematical expression that governs the intensity of these spectral features, which we've alluded to – the Franck-Condon principle.

The intensity of fluorescence at a given frequency ν, denoted $I(\nu)$, is proportional to the square of the absolute value of the overlap integral between the upper vibrational wavefunction and the lower state wavefunction:

$$I(\nu) \propto \left|\langle \psi_{\text{vib}}^{\text{upper}} \mid \psi_E^{\text{lower}} \rangle\right|^2.$$

Let's break this down:

- $\psi_{\text{vib}}^{\text{upper}}$: This is the vibrational wavefunction of the specific vibrational level in the *upper* electronic state from which the emission originates. It's a function of the internuclear coordinates (like R for a diatomic).

- ψ_E^{lower}: This is the wavefunction of the final state in the *lower* electronic state. • If the lower state is bound, then ψ_E^{lower} would be a specific vibrational wavefunction of that bound state. • If the lower state is repulsive or a continuum, then ψ_E^{lower} is a continuum wavefunction characterized by the energy E of the dissociating fragments.

- The notation $\langle \mid \rangle$ represents the integral of the product of these two wavefunctions (with the complex conjugate of the first, if they are complex) over all spatial coordinates. This is the overlap integral.

- The square of the absolute value of this overlap integral gives a quantity proportional to the transition probability.

The slide also reiterates an important consequence: where nodes in $\psi_{\text{vib}}^{\text{upper}}$ exist, they create minima in the fluorescence intensity. A node is a point where the wavefunction passes through zero. If the upper state vibrational wavefunction has a node at a particular internuclear distance R, the overlap integral with lower state wavefunctions that are primarily localized around that R value will be small, leading to a dip or minimum in the fluorescence spectrum corresponding to transitions around that R.

Now we introduce a very important concept on Slide 19: the **Oscillator Strength, denoted f_{ik}**. This concept serves as a bridge between classical ideas of absorption and the quantum mechanical reality.

* Let's start with a **Classical Lorentz oscillator** model. Imagine a single electron of mass m_{e} and charge $-e$, bound to an atomic core by a spring-like force. This electron will have a natural oscillation frequency, ω_0. If light of this frequency ω_0 is incident on this classical oscillator, it will be driven into resonance and will absorb power from the light field. By definition, such an ideal classical oscillator is assigned an **oscillator strength** $f = 1$. It's considered a "perfect" absorber at its resonant frequency.

* Now, a **Real atom** is more complex. An electron in a real atom can make transitions between many different allowed initial states 'i' and final states 'k'. The total "absorbing power" of the electron is, in a sense, distributed among all these possible transitions. The oscillator strength, f_{ik}, for a specific quantum mechanical transition from state 'i' to state 'k', quantifies what fraction of the absorbing power of a single classical electron is associated with this particular transition.

* So, we **Define a dimensionless quantity** f_{ik} such that $N \times f_{ik}$ classical oscillators would mimic the absorption strength of N atoms undergoing the specific transition i to k. In other words, f_{ik} tells us the "effective number" of classical oscillators that corresponds to the quantum mechanical transition i to k. If f_{ik} is, say, 0.5, then the i-to-k transition is half as strong as a classical oscillator. If it's 0.01, it's much weaker. Strong, allowed transitions can have f_{ik} values approaching 1.

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Continuing with the oscillator strength concept:

The N times f_{ik} classical oscillators are conceptualized to mimic the absorption strength of N real atoms when they are undergoing the specific transition from state i to state k. A crucial property of oscillator strengths is the **Sum rule**, specifically the **Thomas-Reiche-Kuhn sum rule**. This rule states that for a given initial state i, the sum of all oscillator strengths, f_{ik}, for transitions to *all possible* final states k (including discrete excited states and the ionization/dissociation continuum) is equal to a constant. For a one-electron atom, this sum is 1.

Mathematically:

$$\sum_k f_{ik} = 1$$

This equation is shown on the slide. The condition mentioned, **"when summation includes continuum,"** is important because transitions to the continuum (ionization for atoms, dissociation for molecules) also contribute to the total oscillator strength.

For multi-electron atoms, the sum rule is slightly more complex: the sum of oscillator strengths from a given level is equal to the number of optically active electrons (valence electrons) involved. The slide simplifies this to 1, which is appropriate for a single active electron system or if f_{ik} is understood as normalized per electron.

The significance of this sum rule is profound: it implies a sort of "conservation of absorption strength." The total ability of an electron to absorb light is fixed, and it's just distributed among various possible transitions. If one transition is very strong (large f_{ik}), others must necessarily be weaker to maintain the sum.

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Slide 20:

Slide 20 delves into the **Physical Meaning and Sign of f_{ik}**, the oscillator strength.

* **For absorption**, which involves a transition from a lower energy state to an upper energy state (lower arrow right upper), the oscillator strength f_{ik} is greater than 0 (positive). This makes sense, as absorption removes energy from the light field.

* **For stimulated emission**, which is a transition from an upper energy state to a lower energy state (upper arrow right lower), the oscillator strength for this process, denoted f_{ki} (for emission from k to i), is related to the absorption oscillator strength f_{ik} by:

$$\mathbf{f_{ki} = -f_{ik}}$$

It's **negative because this process decreases the net absorption of the field energy**; in fact, it adds energy to the field coherently. If we consider the net change in field energy, absorption is positive (loss for field) and stimulated emission is negative (gain for field from the perspective of net absorption). Note that often oscillator strengths are defined as intrinsically positive for both absorption and emission, and their relationship involves degeneracies: $g_i f_{ik}$ (absorption) $=$ $g_k f_{ki}$ (emission). The convention here $f_{ki} = -f_{ik}$ is useful when considering net energy exchange with a field that can cause both processes.

* The magnitude of f_{ik} is also significant: A **Large** f_{ik} implies a strong transition. Strong transitions are characterized by:

* A **short radiative lifetime** of the upper state (if f_{ik} refers to absorption to that state, then f_{ki} for emission from it will also be large, leading to a high Einstein A coefficient). The atom/molecule doesn't stay in the excited state for long.

* A correspondingly **broad natural linewidth**. The natural linewidth is inversely proportional to the lifetime, due to the energy–time uncertainty principle. So, a short lifetime means a larger uncertainty in energy, hence a broader line.

* **Units**: As mentioned before, the oscillator strength f_{ik} is **none (dimensionless)**. This makes it a convenient, universal measure for comparing transition strengths across different atoms, molecules, and spectral regions.

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Slide 21:

Slide 21 gives a concrete **Example: Sodium, specifically the transition** $3\,s\,{}^2S_{\frac{1}{2}}$ to $3\,p\,{}^2P_J$. This refers to the famous sodium D-lines.

The ground state of sodium is $3\,s$, which is a ${}^2S_{\frac{1}{2}}$ state (doublet S one-half). The first excited p-states are $3\,p$, which are split by fine structure into two levels: ${}^2P_{\frac{1}{2}}$ (doublet P one-half) and ${}^2P_{\frac{3}{2}}$ (doublet P three-halves). Transitions from the ground state to these two P levels give the D1 and D2 lines, respectively.

* The slide notes the **Fine-structure split** and gives the oscillator strengths for these two transitions: * For the transition to the $J = \frac{1}{2}$ upper state (i.e., $3\,s\,{}^2S_{\frac{1}{2}} \rightarrow 3\,p\,{}^2P_{\frac{1}{2}}$, which is the D1 line), the oscillator strength f is approximately 0.33 (roughly one-third). * For the transition to the $J = \frac{3}{2}$ upper state (i.e., $3\,s\,{}^2S_{\frac{1}{2}} \rightarrow 3\,p\,{}^2P_{\frac{3}{2}}$, which is the D2 line), the oscillator strength f is approximately 0.66 (roughly two-thirds).

* **Together, the sum of these oscillator strengths is** $0.33 + 0.66 = 0.99$, which is approximately equal to 1. This is a beautiful experimental

confirmation of the Thomas-Reiche-Kuhn sum rule for the single valence electron of sodium. The sum of oscillator strengths for transitions from the $3s$ ground state to these first excited $3p$ states nearly exhausts the total expected sum of 1.

* The **Remaining less than 1% of the oscillator strength** for transitions from the $3s$ state is **distributed among transitions to higher p-states (**$4p$, $5p$, etc.), other types of transitions (e.g., to continuum states via photoionization), and transitions in the far-UV lines. But the vast majority of the absorption strength from the ground state is concentrated in these D-lines.

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This slide highlights the direct **Consequence** of the large oscillator strengths of the sodium D-lines:

- **The Na D lines dominate the optical absorption of sodium vapour.** Because these transitions ($3s$ to $3p$) have oscillator strengths that sum to nearly 1, and they originate from the ground state (which is overwhelmingly populated at typical temperatures), they are by far the strongest absorption features for sodium atoms in the visible and near-UV regions.

This is why:

- Sodium vapor lamps emit their characteristic yellow light (which are these D-lines in emission). - Sodium is so easily detected in flames or astronomical objects via absorption or emission spectroscopy using these lines. - Even trace amounts of sodium can produce significant absorption or emission at these wavelengths.

The concept of oscillator strength provides a quantitative explanation for why certain spectral lines are so prominent.

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Slide 22

Slide 22 shows how we can **Incorporate the oscillator strength,** f_{ik}, Into expressions for Absorption and Dispersion. These equations arise from the classical Lorentz model of an atom interacting with an electromagnetic wave, but with the strength of the interaction now quantified by the quantum mechanical f_{ik}.

* First, the **Macroscopic absorption coefficient for stationary atoms**. The slide denotes this as $\kappa_\mathrm{i}(\omega)$. This κ is related to the imaginary part of the complex refractive index (often $n_{complex} = n' - i\kappa$). The absorption coefficient α (from Beer's Law) is related to this κ by $\alpha = \frac{2\omega\kappa}{c}$.

The expression for $\kappa_\mathrm{i}(\omega)$ is:

$$\kappa_\mathrm{i}(\omega) = \frac{N_\mathrm{i} e^2}{2\epsilon_0 m_\mathrm{e}} \cdot \frac{\omega f_{ik} \gamma_\mathrm{k}}{((\omega_\mathrm{k}^2 - \omega^2)^2 + \gamma_\mathrm{k}^2 \omega^2)}.$$

Let's break this down:

* \` $N_\mathrm{i}$ \` : Number density of atoms in the initial state i. * \` e

$$\epsilon_0$$

$$m_\mathrm{e}$$

$$\omega$$

f_{ik} \` : Oscillator strength for the transition from state $i$ to state $k$. \* \` γ_k \` : Damping constant, related to the FWHM of the natural lineshape of state $k$. \* \` ω_k \` : Resonant angular frequency of the transition i to k.

The denominator structure $((\omega_\mathrm{k}^2 - \omega^2)^2 + \gamma_\mathrm{k}^2 \omega^2)$ is characteristic of a damped harmonic oscillator's response. This expression shows how the absorption strength (via f_{ik}) and line shape (via γ_k and ω_k) are determined.

* Next, the **Real part of the refractive index deviation from unity**, denoted $n'_{\mathrm{i}}(\omega)$. The refractive index itself would be $n(\omega) = n'_{\mathrm{i}}(\omega)$.

$$n'_{\mathrm{i}}(\omega) = 1 + \frac{N_{\mathrm{i}}e^2}{2\epsilon_0 m_{\mathrm{e}}} \cdot \frac{(\omega_{\mathrm{k}}^2 - \omega^2)f_{ik}}{((\omega_{\mathrm{k}}^2 - \omega^2)^2 + \gamma_{\mathrm{k}}^2\omega^2)}.$$

This expression describes how the phase velocity of light changes as it passes through the medium, particularly near an absorption resonance. The characteristic "S-shape" of anomalous dispersion around a resonance is captured by this formula. Again, f_{ik} determines the magnitude of this effect.

These two equations are fundamental in describing how a material responds optically to light, and f_{ik} is central to that response.

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Continuing with the discussion of the expressions for absorption and dispersion:

* The term γ_{k} that appears in these equations is the **full width at half maximum (FWHM) of the natural line shape**. This natural broadening is due to the finite lifetime of the excited state k, a consequence of spontaneous emission, and is related to the Einstein A coefficient. A larger γ_{k} means a broader line.

* An important simplification occurs **Close to resonance**. That is, when the driving frequency ω is very close to the resonant frequency ω_{k}, such that the absolute difference $|\omega - \omega_{\mathrm{k}}|$ is much, much less than ω_{k}. In this near-resonance regime, the somewhat complex frequency-dependent denominators in the expressions for absorption (κ) and dispersion (n') can be simplified. Specifically:

*

$$\omega_{\mathrm{k}}^2 - \omega^2 = (\omega_{\mathrm{k}} - \omega)(\omega_{\mathrm{k}} + \omega) \approx (\omega_{\mathrm{k}} - \omega)(2\omega_{\mathrm{k}})$$

* And in the damping term,

$$\gamma_k^2\omega^2 \approx \gamma_k^2\omega_k^{2.}$$

When these approximations are made, the expressions for absorption (κ) and dispersion (n') **simplify to Lorentzian forms**. The absorption profile becomes a Lorentzian centered at ω_k with FWHM γ_k. The dispersion profile takes on the characteristic derivative-like shape of a Lorentzian dispersion. This Lorentzian approximation is very widely used when analyzing spectra near the center of an isolated absorption line.

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Now we briefly preview another crucial factor influencing spectral lines: the **Influence of Thermal Motion**, which leads to **Doppler Broadening**. This is Slide 23.

* In a gas at a finite **temperature** T, the atoms or molecules are in constant random motion. Their velocities are described by the **Maxwellian velocity distribution**.

* Because of this motion, an atom moving with a velocity component v_z along the direction of light propagation will experience a **Doppler shift**. If the atom is moving towards the light source (or detector), it sees the light frequency blue-shifted (higher). If it's moving away, it sees it red-shifted (lower). The observed (or emitted) frequency in the lab frame, ω', is related to the resonant frequency in the atom's rest frame, ω, by:

$$\omega' = \omega\left(1 + \frac{v_z}{c}\right)$$

where c is the speed of light. v_z is positive if moving towards the detector for an emitter, or away from the source for an absorber.

* The overall observed spectral line shape for an ensemble of moving atoms is then a **Convolution of the Lorentzian (natural) line shape with the**

Gaussian (Doppler) line shape. The Lorentzian arises from the lifetime broadening (γ_k we discussed). The Gaussian arises from the Maxwellian distribution of velocities, which translates into a Gaussian distribution of Doppler shifts. The resulting combined profile is known as a **Voigt profile**. The **effective width** of this Voigt profile, γ_Voigt, can be approximated by the square root of the sum of the squares of the Lorentzian width (γ_k) and a term representing the Doppler width:

$$\gamma_\mathrm{Voigt} \approx \sqrt{\gamma_\mathrm{k}^2 + \left(\frac{\omega_\mathrm{k}\, v_\mathrm{rms}}{c}\right)^2}$$

Here, v_rms is the root-mean-square velocity of the atoms, which depends on temperature and mass. The term $\left(\frac{\omega_\mathrm{k}\, v_\mathrm{rms}}{c}\right)$ is characteristic of the Doppler width (FWHM of the Gaussian component). This approximation is good when one width dominates, or for adding variances.

Doppler broadening is often the dominant broadening mechanism for atomic and molecular transitions in low-pressure gases at visible and UV wavelengths.

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Just a quick note following the preview of Doppler broadening:

* **Later, in Section 3.2 of this course, we will quantify these line broadening effects with exact formulas.**

So, the discussion of the Voigt profile and its width on the previous slide was a brief introduction. We will delve into the mathematical details of line shapes, including natural broadening, Doppler broadening, collisional (pressure) broadening, and the Voigt profile more rigorously in Chapter 3. For now, it's important to be aware that thermal motion significantly affects the observed widths and shapes of spectral lines.

Slide 24

Slide 24 outlines several **Experimental Routes for Measuring Oscillator Strengths (f_{ik})**. Since f_{ik} is such a fundamental quantity, determining its value experimentally is very important.

1. **Absorption or dispersion profile area measurement:**

We've seen equations (like on Slide 43) that relate the absorption coefficient κ (and thus α) and the refractive index n' to the oscillator strength f_{ik}. By carefully measuring the shape of an absorption line ($\alpha(\omega)$) or the dispersion curve ($n'(\omega)$) across a resonance, one can integrate these profiles. The **area under the absorption profile**, for example, $\int \alpha(\omega)\, d\omega$, can be directly related to $N_i f_{ik}$ through the **previously derived equations**. If N_i (the number density of absorbers) is known, f_{ik} can be determined.

2. **Radiative lifetime measurement:**

The radiative lifetime of an excited state k, denoted τ_k, is the average time an atom/molecule spends in that state before spontaneously emitting a photon. This lifetime is directly related to the Einstein A coefficient for spontaneous emission. If state k can only decay to a single lower state i, then the Einstein A coefficient for that specific transition, A_{ki}, equals $\frac{1}{\tau_k}$. (If there are multiple decay channels, then $\frac{1}{\tau_k}$ is the sum of A coefficients for all channels).

There is a direct theoretical relationship between the **Einstein** A coefficient, A_{ki}, and the oscillator strength, f_{ik} (for absorption from i to k, related by $g_i f_{ik} = g_k(\text{constant})A_{ki}$). So, by measuring the lifetime (e.g., using time-resolved fluorescence decay), one can determine A_{ki} and then calculate f_{ik}.

3. **Branching-ratio spectroscopy in combination with a known lifetime τ_k:**

If an excited state k can decay to several different lower states $(i, j, l, \ldots)$, the **branching ratio** for a particular decay channel (say, k to i) is the fraction of decays that proceed through that channel: $\frac{A_{ki}}{(A_{ki}+A_{kj}+A_{kl}+\cdots)}$. The total decay rate is $\frac{1}{\tau_\mathrm{k}} = \left(A_{ki} + A_{kj} + A_{kl} + \cdots\right)$.

If one measures the total lifetime τ_k (giving the sum of A's) and also measures the relative intensities of the fluorescence lines (which are proportional to the A coefficients times populations, or just A's if from the same upper state), one can determine the individual A_{ki} values. Each A_{ki} can then be converted to an oscillator strength f_{ik}.

These methods provide different pathways to experimentally access the fundamental quantity f_{ik}.

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A fourth experimental route for measuring oscillator strengths is:

4. **Laser-induced fluorescence (LIF) with absolute intensity calibration.**

In this method, a laser is used to excite atoms or molecules to a specific upper state. The subsequent fluorescence emission is collected and its intensity is measured. If the measurement of the fluorescence intensity is *absolute* (i.e., calibrated to give the actual number of photons emitted per unit time per unit volume), and if the number density of excited atoms created by the laser is known or can be determined, then one can directly calculate the Einstein A coefficient for the observed fluorescence transition.

This A coefficient is then related to the oscillator strength f_{ik}, as discussed before.

Achieving accurate absolute intensity calibration can be challenging, requiring careful characterization of the collection optics efficiency, detector quantum efficiency, and the geometry of the fluorescence collection. However, when done carefully, it's a powerful method.

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This slide shows a schematic diagram of an **Experimental Setup for Measuring Oscillator Strength (f)** via Laser Absorption Spectroscopy. This is a common and fundamental technique.

Let's trace the components:

* At the far left, we have a **Tunable Laser**. This provides the source of monochromatic light whose wavelength can be scanned across the absorption line of interest.

* The laser beam passes through a **Beam Splitter (BS)**. *A portion of the beam (the main beam) goes straight through towards the sample. This beam passes through an **I Detector** (Intensity Detector)* before* the sample, which can be used to measure the incident intensity, I_0, or this I_0 detector could be after the beam splitter in the reference arm. The diagram shows an "I Detector" after the sample, so let's assume I_0 is measured by the reference arm. * The beam then passes through the **Absorption Cell**. This cell contains the sample (e.g., a gas) characterized by its number density N (or N_i) and path length L. * After the absorption cell, the transmitted light intensity, I, is measured by another **I Detector**.

* The second beam path, created by the beam splitter, forms a reference arm. This beam goes directly to an **I Detector**, labeled as "Reference Cavity (Frequency Markers)" feeding into a "Cavity Detector". More typically, a small portion of the main laser beam is split off and sent through a **Reference Cavity**, such as a Fabry-Pérot etalon. As the laser frequency is scanned, this cavity transmits light only at specific resonant frequencies, providing a set of

Frequency Markers. A **Cavity Detector** measures these transmission peaks. This allows for precise calibration of the laser frequency scan.

* The signals from all detectors (measuring I, I_0 implicitly or via reference, and frequency markers) are fed into a **Data Acquisition & Control** system. This system records the data and may also control the laser tuning.

By measuring $I(\nu)$ and $I_0(\nu)$ as a function of frequency (ν), one can calculate the absorbance or the absorption coefficient $\alpha(\nu)$. Integrating $\alpha(\nu)$ across the line profile, and knowing N and L, allows for the determination of the oscillator strength f, as per the relationships we've discussed.

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Slide 25 presents the Starting Point for deriving the $B_{ik} - \sigma_{ik}$ Relation**, that is, the relationship between the Einstein** B coefficient and the absorption cross section.

We consider a **dilute sample**, which implies that the population of the upper state, N_k, is approximately zero ($N_\mathrm{k} \approx 0$). In this case, stimulated emission can be neglected. The **excitation rate**, or more accurately, the power absorbed $\frac{dW_{ik}}{dt}$ due to stimulated absorption, is given by:

$$\frac{dW_{ik}}{dt} = N_\mathrm{i}\, B_{ik}\, \rho(\omega)\, \hbar\omega\, \Delta V.$$

Let's break this down:

- $\frac{dW_{ik}}{dt}$: Power absorbed in volume ΔV.

- N_i: Number density of atoms in the lower state i.

- B_{ik}: Einstein B coefficient for stimulated absorption from i to k (defined here with respect to angular frequency energy density $\rho(\omega)$).

- $\rho(\omega)$: Spectral energy density of the incident radiation field at angular frequency ω (Energy per unit volume per unit angular frequency interval).

- $\hbar\omega$: Energy of a single photon.

- ΔV: Volume of the sample interacting with the radiation.

This equation states that the absorbed power is proportional to the number of absorbers, the B coefficient, the energy density of the field, and the photon energy.

Next, the **Plane wave energy density** $\rho(\omega)$ is related to the spectral intensity $I(\omega)$ (power per unit area per unit angular frequency for a beam) by:

$$I(\omega) = c\,\rho(\omega),$$

where c is the speed of light. This relationship allows us to switch between descriptions based on energy density (often used in theoretical derivations of B coefficients) and intensity (often measured in experiments).

The **Goal** is to **express** B_{ik} in terms of the experimentally accessible absorption coefficient α_{ik} of ω (or the related absorption cross section σ_{ik} of ω). This will provide a bridge between the fundamental Einstein coefficient and measurable quantities.

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Slide 26 outlines the **Full Derivation of Equation 2.64** (this equation number likely refers to a textbook). This derivation aims to connect the macroscopic absorption with the microscopic Einstein B coefficient.

1. **Express absorbed power differential:**

The power absorbed from a beam of spectral intensity $I(\omega)$ within a spectral bandwidth $d\omega$ as it passes through a sample of volume ΔV with an absorption coefficient $\alpha_{ik}(\omega)$ is given by:

$$dP(\omega) = I(\omega) \times \alpha_{ik}(\omega) \times \mathit{\Delta} V \times d\omega.$$

Here, $dP(\omega)$ is the power absorbed from the spectral interval $d\omega$. $\alpha_{ik}(\omega)$ is the absorption coefficient (per unit length), so $\alpha_{ik}(\omega) \times \mathit{\Delta} V$ implicitly involves multiplying by a length if $\mathit{\Delta} V$ is Area × length. More directly,

\[dP(\omega) = I(\omega) *\alpha_{ik}(\omega)* \text{Area} *d(\text{length})* d\omega.\]

So power absorbed in volume $\mathit{\Delta} V$ from bandwidth $d\omega$ is

\[\frac{I(\omega) \alpha_{ik}(\omega) \Delta V d\omega}{\text{Area} *d(\text{length})}* \text{Area} * d(\text{length}).\]

Yes, this is consistent.

2. **Integrate across the full spectral line:**

To find the total power absorbed, P_{tot}, we integrate this differential power over all frequencies (or angular frequencies) where $\alpha_{ik}(\omega)$ is non-zero:

$$P_{tot} = \mathit{\Delta} V \times \int_{0}^{+\infty} I\,(\omega) \times \alpha_{ik}(\omega) \times d\omega.$$

The integration limit can be taken from 0 to $+\infty$ as alpha is typically only non-zero around positive resonant frequencies. If $I(\omega)$ is broadband and varies slowly across the absorption line, it can be approximated as $I(\omega_{ik})$ and taken out of the integral.

3. **Equate with Einstein form at steady state:**

This macroscopic P_{tot} must be equal to the power absorbed as described by the Einstein B coefficient. The Einstein form for absorbed power is given as:

$$N_{\mathrm{i}} \times B_{ik} \times \rho(\omega_{ik}) \times \hbar\omega_{ik} \times \mathit{\Delta} V.$$

This is the expression we saw on the previous slide (assuming $N_{\mathrm{k}} = 0$). It's stated that this equating happens "at steady state where stimulated rate equals integrated absorption." This phrasing usually applies when considering saturation, but here, for $N_\mathrm{k} = 0$, it simply means equating the two descriptions of absorbed power. We are equating the total power absorbed, integrated over the line, with the power absorption rate described by the B coefficient acting with the energy density at the line center (or assuming B already incorporates the line shape if ρ is broadband).

This procedure will allow us to solve for B_{ik}.

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Following the steps from the previous slide, we now **Solve for** B_{ik}.

By equating the two expressions for total absorbed power (P_tot from integrating $I\,\alpha\,dV\,d\omega$, and P_tot from the Einstein B coefficient formulation), and using the relation $I(\omega) = c\,\rho(\omega)$, we arrive at the following expression for B_{ik}:

$$B_{ik} = \frac{2\pi c}{N_\mathrm{i}\,\hbar\,\omega_{ik}} \int_0^\infty \alpha_{ik}\,(\omega)\,d\omega.$$

Let's analyze this expression and the note about the 2π factor.

If B_{ik} here is $B_{ik}^{(\omega)}$ (defined for angular frequency energy density ρ_ω), and we use $\alpha_{ik}(\omega) = N_\mathrm{i}\,\sigma_{ik}(\omega)$ (for $N_\mathrm{k} = 0$), then the previous derivation (page 25) yielded:

$$B_{ik}^{(\omega)} = \frac{c}{\hbar\,\omega_{ik}} \int \sigma_{ik}(\omega)\,d\omega = \frac{c}{N_\mathrm{i}\,\hbar\,\omega_{ik}} \int \alpha_{ik}(\omega)\,d\omega.$$

This form does *not* have the 2π factor.

The slide provides a note: **"where factor** 2π converts from $d\nu$ to $d\omega = 2\pi\,d\nu$."

This suggests that the B_{ik} being solved for might be $B_{ik}^{(\nu)}$ (for frequency ν and energy density ρ_ν), while the integral is over $d\omega$.

We know that $B_{ik}^{(\omega)} = B_{ik}^{(\nu)}$ is not the standard relation. The rates must be equal:

$$B_{ik}^{(\nu)}\,\rho_\nu = B_{ik}^{(\omega)}\,\rho_\omega.$$

Since $\rho_\nu\,d\nu = \rho_\omega\,d\omega$ and $d\omega = 2\pi\,d\nu$, we have $\rho_\nu = 2\pi\,\rho_\omega$.

Therefore,

$$B_{ik}^{(\nu)}\,(2\pi\,\rho_\omega) = B_{ik}^{(\omega)}\,\rho_\omega,$$

which implies

$$B_{ik}^{(\omega)} = 2\pi\,B_{ik}^{(\nu)}.$$

So, if the B_{ik} on the slide is $B_{ik}^{(\nu)}$, then:

$$B_{ik}^{(\nu)} = \frac{B_{ik}^{(\omega)}}{2\pi} = \frac{1}{2\pi}\,\frac{c}{N_\mathrm{i}\,\hbar\,\omega_{ik}}\int \alpha_{ik}(\omega)\,d\omega.$$

This form has $\frac{1}{2\pi}$, not 2π.

However, if the integral was $\int \alpha_{ik}(\nu)\,d\nu$, then:

$$B_{ik}^{(\nu)} = \frac{c}{N_\mathrm{i}\,h\,\nu_{ik}}\int \alpha_{ik}(\nu)\,d\nu.$$

And

$$\int \alpha_{ik}(\omega)\,d\omega = \int \alpha_{ik}(\nu)\,\frac{d\omega}{d\nu}\,d\nu = 2\pi\int \alpha_{ik}(\nu)\,d\nu.$$

So

$$\int \alpha_{ik}(\nu)\,d\nu = \frac{1}{2\pi}\int \alpha_{ik}(\omega)\,d\omega.$$

Substituting this into the $B_{ik}^{(\nu)}$ expression:

$$B_{ik}^{(\nu)} = \frac{c}{N_\mathrm{i}\, h\, \nu_{ik}} \cdot \frac{1}{2\pi} \int \alpha_{ik}(\omega)\, d\omega.$$

Since $h\nu_{ik} = \hbar\, \omega_{ik}$, this is

$$B_{ik}^{(\nu)} = \frac{c}{N_\mathrm{i}\, \hbar\, \omega_{ik}\, 2\pi} \int \alpha_{ik}(\omega)\, d\omega.$$

This still results in $\frac{1}{2\pi}$.

The expression on the slide,

$$B_{ik} = \frac{2\pi c}{N_\mathrm{i}\, \hbar\, \omega_{ik}} \int \alpha_{ik}(\omega)\, d\omega,$$

appears to be for a B_{ik} that is $(2\pi)^2$ times larger than my derived $B_{ik}^{(\nu)}$ in terms of the ω integral, or there's a specific convention for B_{ik} and α_{ik} being used.

Given the final well-known result on slide 54, we should aim for the standard $B_{ik}^{(\omega)}$. The formula for $B_{ik}^{(\omega)}$ should be

$$\frac{c}{N_\mathrm{i}\, \hbar\, \omega_{ik}} \int \alpha_{ik}(\omega)\, d\omega.$$

The 2π factor here is likely an error or relates to a non-standard definition of B or α. For the purpose of this lecture, we will note this formula and proceed, as the final connection to oscillator strength is standard and correct.

Page 53:

Now, on Slide 27, we are **Substituting the Lorentz Oscillator Model** into our framework. This is a key step to connect the Einstein B_{ik} coefficient with the oscillator strength f_{ik}.

- The first step is to **Insert** $\alpha_{ik}(\omega) = \frac{2\omega}{c}\kappa_i(\omega)$. Here, $\alpha_{ik}(\omega)$ is the absorption coefficient, and $\kappa_i(\omega)$ is the imaginary part of the complex refractive index, whose expression (containing f_{ik}) was given on Slide 43. The expression for $\kappa_i(\omega)$ from Slide 43 was:

$$\kappa_i(\omega) = \frac{N_{\mathrm{i}} e^2}{2\epsilon_0 m_{\mathrm{e}}} \cdot \frac{\omega\, f_{ik}\, \gamma_{\mathrm{k}}}{(\omega_{\mathrm{k}}^2 - \omega^2)^2 + \gamma_{\mathrm{k}}^{2\,\omega^2}}$$

So,

$$\alpha_{ik}(\omega) = \frac{2\omega}{c} \cdot \frac{N_{\mathrm{i}} e^2}{2\epsilon_0 m_{\mathrm{e}}} \cdot \frac{\omega\, f_{ik}\, \gamma_{\mathrm{k}}}{(\omega_{\mathrm{k}}^2 - \omega^2)^2 + \gamma_{\mathrm{k}}^{2\,\omega^2}}$$

$$\alpha_{ik}(\omega) = \frac{N_{\mathrm{i}} e^2}{\epsilon_0 m_{\mathrm{e}} c} \cdot \frac{\omega^2\, f_{ik}\, \gamma_{\mathrm{k}}}{(\omega_{\mathrm{k}}^2 - \omega^2)^2 + \gamma_{\mathrm{k}}^{2\,\omega^2}}$$

This is a standard expression for the absorption coefficient from the Lorentz model.

- Next, we need to **Compute the integral** $\int_0^{+\infty} \alpha_{ik}\,(\omega)\, d\omega$ analytically. This involves integrating the expression for $\alpha_{ik}(\omega)$ we just wrote down. This integral, while looking complicated, can be solved, often using approximations valid near resonance (where $\omega \approx \omega_{\mathrm{k}}$) or by contour integration. A common approximation for the integral of a Lorentzian-like function $\int \frac{A\gamma}{(\omega_0-\omega)^2+(\gamma/2)^2}\, d\omega \approx A\pi.$ The integral

$$\int_0^{\infty} \frac{\omega^2\, \gamma_{\mathrm{k}}\, d\omega}{(\omega_{\mathrm{k}}^2 - \omega^2)^2 + \gamma_{\mathrm{k}}^{2\,\omega^2}}$$

when $\gamma_{\mathrm{k}} \ll \omega_{\mathrm{k}}$ (narrow line approximation) evaluates to $\pi/2$. So,

$$\int_0^{\infty} \alpha_{ik}\,(\omega)\, d\omega \approx \frac{N_{\mathrm{i}} e^2}{\epsilon_0 m_{\mathrm{e}} c} \cdot f_{ik} \cdot \omega_{\mathrm{k}}^{2\cdot} \gamma_{\mathrm{k}} \cdot \text{(integral part)}$$

The actual result for the integral $\int_0^{\infty} \alpha_{ik}\,(\omega)\, d\omega$ is

$$\frac{N_{\mathrm{i}}\pi e^2}{2\epsilon_0 m_{\mathrm{e}} c} f_{ik}$$

.

- The slide presents an intermediate integral: **Integral from 0 to plus infinity of** $\left[\frac{\omega\,\gamma_{ik}\,d\omega}{\left(\left(\omega_{ik}^2-\omega^2\right)^2+\frac{1}{4}\gamma_{ik}^2\,\omega^2\right)}\right]$ equals $2\pi\,\omega_{ik}$. This specific integral form and its result $2\pi\,\omega_{ik}$ are unusual and seem to be part of a very specific derivation path or contain typos. The standard integration of $\alpha(\omega)$ from the Lorentz model gives the $\frac{N_{\mathrm{i}}\pi e^2}{2\epsilon_0 m_{\mathrm{e}} c} f_{ik}$ result.
- The aim is to **Obtain an elegant relationship** between B_{ik} and f_{ik}.

Page 54:

After performing the integration of $\alpha_{ik}(\omega)$ (which contains f_{ik}) and substituting it into the expression for $B_{ik}^{(\omega)}$ (which was $B_{ik}^{(\omega)} = \frac{c}{N_{\mathrm{i}}\hbar\omega_{ik}}\int \alpha_{ik}(\omega)\,d\omega$), we arrive at the following fundamental and elegant relationship:

$$B_{ik}^{(\omega)} = \frac{\pi e^2}{2m_{\mathrm{e}}\epsilon_0\hbar\omega_{ik}} f_{ik}$$

Let's break down the terms in this crucial equation:

- $B_{ik}^{(\omega)}$: This is the Einstein B coefficient for stimulated absorption (or emission, related by degeneracies) for the transition i to k, defined with respect to the angular frequency energy density $\rho(\omega)$.
- π: The mathematical constant pi.
- e: The elementary charge.
- m_{e}: The mass of the electron.

- ϵ_0: The permittivity of free space.
- $\hbar$: The reduced Planck constant (h divided by 2π).
- ω_{ik}: The resonant angular frequency of the transition i to k.
- f_{ik}: The dimensionless oscillator strength of the transition i to k.

This equation provides a direct link between the quantum mechanical Einstein B coefficient, which describes transition probabilities, and the semi-classical oscillator strength, which quantifies the "strength" of a transition. It shows that B_{ik} is directly proportional to f_{ik}.

The slide also notes an **Important conversion** between B coefficients defined for angular frequency (ω) and those for linear frequency (ν):

$$B_{ik}^{(\nu)} = \frac{B_{ik}^{(\omega)}}{2\pi}$$

This conversion arises **because the energy densities are related by** $\rho(\nu) = 2\pi\rho(\omega)$.

To see this: the rate of transitions must be independent of the units used, so

$$\text{Rate} = B_{ik}^{(\nu)}\rho(\nu) = B_{ik}^{(\omega)}\rho(\omega)$$

Substituting $\rho(\nu) = 2\pi\rho(\omega)$ gives

$$B_{ik}^{(\nu)}\big(2\pi\rho(\omega)\big) = B_{ik}^{(\omega)}\rho(\omega)$$

This implies $B_{ik}^{(\omega)} = 2\pi B_{ik}^{(\nu)}$, or $B_{ik}^{(\nu)} = \frac{B_{ik}^{(\omega)}}{2\pi}$. This conversion is correct.

This relationship between B_{ik} and f_{ik} is a cornerstone for linking theoretical calculations of transition strengths with experimental measurements.

Page 55:

Slide 28:

Slide 28 introduces another important quantity related to the strength of an absorption line: the **Integrated Absorption — Line Strength** S_{ik}.

* We **Define the line strength,** S_{ik}, as the integral of the absorption cross section, σ_{ik}, over the entire spectral line. It can be defined with respect to angular frequency ω or linear frequency ν:

$S_{ik} = \int_0^{+\infty} \sigma_{ik}\,(\omega)\, d\omega\; S_{ik} = \int_0^{+\infty} \sigma_{ik}\,(\nu)\, d\nu$

It's important to be careful here: $\sigma_{ik}(\omega)$ and $\sigma_{ik}(\nu)$ are different functions, related by $\sigma_{ik}(\omega)\, d\omega = \sigma_{ik}(\nu)\, d\nu$. Since $d\omega = 2\pi\, d\nu$, it means $\sigma_{ik}(\omega) = \frac{\sigma_{ik}(\nu)}{2\pi}$.

Therefore, $S_{ik}^{(\omega)} = \int \sigma_{ik}(\omega)\, d\omega$ and $S_{ik}^{(\nu)} = \int \sigma_{ik}(\nu)\, d\nu$ are related by $S_{ik}^{(\omega)} = S_{ik}^{(\nu)}$. This seems incorrect.

Let's define $S_{ik}^{(\omega)} = \int \sigma_{ik}(\omega)\, d\omega$ and $S_{ik}^{(\nu)} = \int \sigma_{ik}(\nu)\, d\nu$.

Since $\sigma_{ik}(\omega)\, d\omega = \sigma_{ik}(\nu)\, d\nu$ is not true, but rather the *number of absorbed photons* in corresponding intervals should be proportional.

The absorption cross section σ is an area. The integrated absorption cross section should have units of Area × Frequency.

So, $S_{ik}^{(\omega)}$ has units of **meters squared times radians per second (m^2 rad/s)**.

And $S_{ik}^{(\nu)}$ has units of **meters squared times Hertz (m^2 Hz)**, or equivalently **meters squared per second (m^2 s^{-1})** since Hz is s^{-1}.

The relation is $S_{ik}^{(\omega)} = 2\pi\, S_{ik}^{(\nu)}$. The slide equating them means S_{ik} is being used generically.

* Now, the **Relation to** $B_{ik}^{(\omega)}$.

We had (from page 25, assuming $h\nu$ there meant $\hbar\omega_{ik}$):

$$B_{ik}^{(\omega)} = \frac{c}{\hbar\omega_{ik}} \int \sigma_{ik}(\omega)\, d\omega.$$

So, if $S_{ik}^{(\omega)} = \int \sigma_{ik}(\omega)\, d\omega$, then:

$$B_{ik}^{(\omega)} = \frac{c}{\hbar\omega_{ik}} S_{ik}^{(\omega)}.$$

The slide presents: $B_{ik}^{(\omega)} = \frac{2\pi\, c}{\hbar\omega_{ik}} S_{ik}$.

For this to be consistent with $B_{ik}^{(\omega)} = \frac{c}{\hbar\omega_{ik}} S_{ik}^{(\omega)}$, the S_{ik} on this slide must be $\frac{S_{ik}^{(\omega)}}{2\pi}$, which is $S_{ik}^{(\nu)}$.

So, if S_{ik} here represents $S_{ik}^{(\nu)} = \int \sigma_{ik}(\nu)\, d\nu$, then the formula

$$B_{ik}^{(\omega)} = \frac{2\pi\, c}{\hbar\omega_{ik}} S_{ik}^{(\nu)}$$

is correct because $\hbar\omega_{ik} = h\nu_{ik}$ and $S_{ik}^{(\omega)} = 2\pi\, S_{ik}^{(\nu)}$. This connects the B coefficient to the integrated cross section defined in terms of linear frequency.

Line strength S_{ik} is a very useful quantity as it represents the total strength of a transition, independent of broadening effects that might change the line's shape but not its total area.

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This slide makes a practical point regarding the measurement of these quantities:

* The **"Area under the cross-section curve"**, which is precisely what the line strength S_{ik} (the integrated absorption cross section) represents, **is easier to measure experimentally than the Einstein B coefficient,** B_{ik}, directly.

Why is this the case?

To determine S_{ik}, one typically measures the absorption spectrum $\alpha(\nu)$ or $\sigma(\nu)$ over the entire line profile. Even if the line is broadened by various mechanisms (Doppler, collisional), as long as the entire profile is captured, the area under it gives S_{ik} (or $\int \alpha \, d\nu$, which is $N_{\mathrm{i}} \, S_{ik}$). This measurement relies on relative intensity changes (I/I_0) and frequency calibration.

Directly measuring B_{ik} would require accurately knowing the spectral energy density $\rho(\omega)$ of the light interacting with the atoms, along with precise measurements of population densities and transition rates, which can be more challenging. Since S_{ik} is derivable from standard absorption spectra and is directly related to B_{ik}, it provides a more convenient experimental route to quantify fundamental transition probabilities.

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Slide 29 introduces the concept of an **Averaged Absorption Cross Section, denoted** $\bar{\sigma}_{ik}$. This provides another way to characterize the strength of a line, especially in relation to its observed width.

- First, we consider the **Experimental linewidth**. This is often characterized by the **half-width-at-half-maximum (HWHM)**, which the slide denotes as $\Delta\nu$. (Note: sometimes $\Delta\nu$ is used for FWHM, so clarity is important. Here, it's specified as HWHM).

- We then **Define** $\bar{\sigma}_{ik}$ as:

$$\bar{\sigma}_{ik} = \frac{1}{\Delta\nu} \int_{\text{line}} \sigma_{ik} \, (\nu) \, d\nu.$$

The integral $\int_{\text{line}} \sigma_{ik} \, (\nu) \, d\nu$ is precisely the line strength $S_{ik}^{(\nu)}$. So, this definition states that the averaged absorption cross section is the total line strength $S_{ik}^{(\nu)}$ divided by the HWHM linewidth $\Delta\nu$. $\bar{\sigma}_{ik} = \frac{S_{ik}^{(\nu)}}{\Delta\nu_{\text{HWHM}}}$. This $\bar{\sigma}_{ik}$ effectively represents the average strength of the cross section across the HWHM of the line.

- From this definition, it follows directly that **Then**:

$$S_{ik} = \Delta\nu \cdot \bar{\sigma}_{ik}.$$

(Here S_{ik} is $S_{ik}^{(\nu)}$ and $\Delta\nu$ is $\Delta\nu_{HWHM}$). This means the total area under the line (line strength) can be thought of as the product of an effective average height ($\bar{\sigma}_{ik}$) and an effective width ($\Delta\nu$).

- The utility of this concept is that it **Combines the ease of measuring peak width and integrated area.** Experimentally, it can be easier to determine a characteristic linewidth (like FWHM or HWHM from the spectral profile) and relate it to the total integrated area rather than dealing with the detailed line shape function at every point, especially if the exact line shape is complex (e.g., Voigt). However, note that $\bar{\sigma}_{ik}$ defined this way is not necessarily the peak cross section, $\sigma_{ik}(\nu_0)$, unless the line shape is rectangular. For a Lorentzian, FWHM is γ, and peak is $\frac{S}{\pi\,(\gamma/2)}$.

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Slide 30 focuses on **Linking the averaged absorption cross section,** $\bar{\sigma}_{ik}$, to the Einstein A coefficient, A_{ik}. This provides a connection between a measurable absorption parameter and a fundamental emission parameter.

* The slide starts with a formula for the Einstein A coefficient, presumably A_{ki} (for spontaneous emission from k to i), in terms of the oscillator strength f_{ik} (for absorption i to k):

$$A_{ik} = \frac{8\pi^2\nu_{ik}^2 e^2}{m_{\mathrm{e}} c^3 \epsilon_0}\, f_{ik}$$

This formula relates A_{ki} to f_{ik}. A standard relation is

$$g_{\mathrm{k}} A_{ki} = g_{\mathrm{i}} \left(\frac{8\pi^2 e^2 \nu_{ik}^2}{m_{\mathrm{e}} c^3 \epsilon_0} \right) f_{ik}$$

If $g_{\mathrm{i}} = g_{\mathrm{k}}$, this matches if A_{ik} on the slide is A_{ki}. Let's assume this relation as given.

* Then, by **Substituting and simplifying**, using previous relations between f_{ik}, B_{ik}, S_{ik}, and $\bar{\sigma}_{ik}$, a relationship for $\bar{\sigma}_{ik}$ is provided:

$$\bar{\sigma}_{ik} = \frac{\lambda_{ik}^2 A_{ik}}{8\pi \Delta\nu}$$

Let's try to verify this. We had

$$S_{ik}^{(\nu)} = \Delta\nu_{HWHM}\, \bar{\sigma}_{ik}$$

(if $\Delta\nu$ is HWHM).

And

$$S_{ik}^{(\nu)} = \frac{g_{\mathrm{k}}}{g_{\mathrm{i}}} \frac{\lambda_{ik}^2}{8\pi} A_{ki}$$

is a standard formula relating line strength to Einstein A coefficient.

So,

$$\bar{\sigma}_{ik} = \frac{S_{ik}^{(\nu)}}{\Delta\nu_{HWHM}} = \frac{\frac{g_{\mathrm{k}}}{g_{\mathrm{i}}} \frac{\lambda_{ik}^2}{8\pi} A_{ki}}{\Delta\nu_{HWHM}}$$

This matches the slide's formula if A_{ik} on the slide is taken as $\left(\frac{g_{\mathrm{k}}}{g_{\mathrm{i}}}\right) A_{ki}$ or if $g_{\mathrm{i}} = g_{\mathrm{k}}$ and A_{ik} is A_{ki}, and $\Delta\nu$ is the HWHM.

This equation is very useful because it connects the averaged absorption cross section (measurable from an absorption lineshape and its width) to the Einstein A coefficient (related to radiative lifetime and fundamental emission properties) and the wavelength of the transition. $\Delta\nu$ here is the observed HWHM, which could be due to various broadening mechanisms.

Page 59:

This slide considers a very important special case:

If the linewidth is limited solely by spontaneous emission, meaning we are looking at the **natural width** of the line. The natural linewidth (FWHM in Hz) is given by $\Delta\nu_{nat\_\mathrm{FWHM}} = \frac{A_\mathrm{k}}{2\pi}$, where A_k is the total spontaneous emission rate from the upper state k. If state k decays only to state i, then $A_\mathrm{k} = A_{ki}$.

The slide denotes the natural width (presumably HWHM if $\Delta\nu$ was HWHM on previous slide) as:

$\Delta\nu_\mathrm{n} = \frac{A_{ik}}{2\pi}$. (Let's assume A_{ik} is A_{ki} and this is FWHM. If $\Delta\nu$ on prev. slide was HWHM, then this should be HWHM too $\frac{A_{ki}}{4\pi}$ or the previous $\Delta\nu$ was FWHM).

If we substitute this natural FWHM linewidth $\Delta\nu = \frac{A_{ki}}{2\pi}$ into the formula for $\bar{\sigma}_{ik}$ from the previous page (assuming $g_\mathrm{i} = g_\mathrm{k}$):

$$\bar{\sigma}_{ik} = \frac{\frac{\lambda_{ik}^2}{8\pi} A_{ki}}{\Delta\nu}$$

If $\Delta\nu$ here is the FWHM $\frac{A_{ki}}{2\pi}$, then

$$\bar{\sigma}_{ik}^{\mathrm{natural}} = \frac{\frac{\lambda_{ik}^2}{8\pi} A_{ki}}{\frac{A_{ki}}{2\pi}} = \frac{\lambda_{ik}^2 A_{ki}\, 2\pi}{8\pi A_{ki}} = \frac{\lambda_{ik}^2}{4}$$

The slide gives the result for the averaged cross section under these conditions (presumably the peak cross section for a naturally broadened line):

$$\bar{\sigma}_{ik}^{\text{natural}} = \frac{\lambda_{ik}^2}{4}$$

This result, $\frac{\lambda^2}{4}$, is indeed a well-known expression for the peak absorption cross section of a transition that is only broadened by its natural lifetime, assuming equal degeneracies for the initial and final states and that the "averaged" cross section is interpreted as the peak of the Lorentzian.

This result is **strikingly independent of A_{ik}.** Although A_{ik} (the spontaneous emission rate) determines the natural linewidth, it cancels out when calculating this peak cross section. A larger A_{ik} leads to a proportionally larger integrated line strength S_{ik} AND a proportionally larger natural linewidth. The ratio, which gives the peak cross section, depends only on the wavelength of the transition. This is a very elegant and fundamental result in spectroscopy.

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Slide 31 provides a Numerical Example – the Sodium D-Line **– to illustrate these concepts.**

- The **Wavelength,** λ, for the sodium D-line is approximately 589 nanometers (nm).
- **Using the formula for the peak natural absorption cross section,** $\bar{\sigma}_{ik}^{\text{natural}} = \frac{\lambda^2}{4}$:

The slide shows the calculation:

$$(589 \times 10^{-9}\ \text{m})^2 \div 4 = 9 \times 10^{-18}\ \text{m}^2 = 9 \times 10^{-10}\ \text{cm}^{2.}$$

Let's check this calculation:

$$\lambda = 589\,\text{nm} = 5.89 \times 10^{-7}\,\text{m}.$$

$$\lambda^2 = (5.89 \times 10^{-7})^2\,\text{m}^2 = 34.6921 \times 10^{-14}\,\text{m}^{2.}$$

$$\frac{\lambda^2}{4} = \frac{34.6921 \times 10^{-14}}{4}\,\text{m}^2 = 8.673 \times 10^{-14}\,\text{m}^{2.}$$

This is

$$8.673 \times 10^{-10}\,\text{cm}^{2.}$$

The value on the slide, $9 \times 10^{-18}\,\text{m}^2$, appears to be incorrect by several orders of magnitude if the formula $\frac{\lambda^2}{4}$ is used. $9 \times 10^{-18}\,\text{m}^2$ would correspond to a much shorter wavelength.

However, if the subsequent calculations rely on the slide's value for $\bar{\sigma}_{ik}$, we will proceed with that, noting the discrepancy. It's possible the $\frac{\lambda^2}{4}$ is an ideal case and the $9 \times 10^{-18}\,\text{m}^2$ is a more realistic or differently defined value for this specific example. For the purpose of following the lecture's flow, let's assume

$$\bar{\sigma}_{ik} = 9 \times 10^{-10}\,\text{cm}^2$$

(which is $9 \times 10^{-14}\,\text{m}^2$, closer to our calculation, but the slide explicitly states

$$9 \times 10^{-18}\,\text{m}^2 = 9 \times 10^{-10}\,\text{cm}^{2,}$$

which implies $1\,\mathrm{m}^2 = 10^8\,\mathrm{cm}^2$, an error since $1\,\mathrm{m}^2 = 10^4\,\mathrm{cm}^2$. If $9 \times 10^{-18}\,\mathrm{m}^2$ is the starting point, then it would be $9 \times 10^{-14}\,\mathrm{cm}^2$.)

Given the final result on the next slide ($\alpha = 2\,\mathrm{cm}^{-1}$), it seems the intended cross section is around $0.8 \times 10^{-10}\,\mathrm{cm}^2$.

Let's assume the value

$$\bar{\sigma}_{ik} = 9 \times 10^{-10}\,\mathrm{cm}^2$$

is what the slide *intends* to use for the next step, regardless of the $\frac{\lambda^2}{4}$ calculation's accuracy or the m^2 to cm^2 conversion error on the slide.

- Next, a **Vapour pressure of** 10^{-6} mbar for sodium is considered. This vapour pressure corresponds to a certain **number density** N_i (assuming most sodium atoms are in the ground state 'i'). The slide states this number density as:

$$N_\mathrm{i} = 2.5 \times 10^{10}\,\mathrm{atoms/cm}^{3.}$$

This conversion from pressure to number density would use the ideal gas law,

$$P = \frac{N k_\mathrm{B} T}{V}$$

or

$$\frac{N}{V} = \frac{P}{k_\mathrm{B} T}.$$

$(10^{-6}$ mbar $= 0.1$ Pa. At $T \sim 400\text{-}500$ K for this vapor pressure, N_i can be calculated).

- With N_i and $\bar{\sigma}_{ik}$, we can now calculate the **Absorption coefficient**, which will be on the next slide.

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Continuing the numerical example for the Sodium D-line:

We have the number density $N_\text{i} = 2.5 \times 10^{10}$ cm^{-3}.

And from the previous slide, if we use their stated $\bar{\sigma}_{ik} = 9 \times 10^{-10}$ cm^2.

Then the absorption coefficient, α_{ik}, is calculated as $N_\text{i} \times \bar{\sigma}_{ik}$:

$$\alpha_{ik} = (2.5 \times 10^{10}\ \text{cm}^{-3}) \times (9 \times 10^{-10}\ \text{cm}^2)$$

This product is $2.5 \times 9 = 22.5$ per centimeter (cm^{-1}).

However, the slide gives the result as: $= 2$ cm^{-1}.

For α_{ik} to be 2 cm^{-1} with $N_\text{i} = 2.5 \times 10^{10}$ cm^{-3}, the cross section $\bar{\sigma}_{ik}$ would need to be:

$$\bar{\sigma}_{ik} = \frac{\alpha_{ik}}{N_\text{i}} = \frac{2\ \text{cm}^{-1}}{2.5 \times 10^{10}\ \text{cm}^{-3}} = 0.8 \times 10^{-10}\ \text{cm}^2$$

This value 0.8×10^{-10} cm^2 (or 8×10^{-15} m^2) is different from the 9×10^{-10} cm^2 given on the previous slide, and also from our $\lambda^2/4$ calculation ($\sim 8.67 \times 10^{-10}$ cm^2).

There seems to be some inconsistency in the numerical values presented across these example calculation steps. However, let's proceed with the slide's final result for alpha.

* Assuming the absorption coefficient α_{ik} is indeed 2 cm^{-1}: **Hence, the intensity of light passing through this sodium vapor attenuates by a factor**

of e^{-1} after a path length of $0.5\,\mathrm{cm}$. This comes from Beer's Law: $I = I_0 \exp(-\alpha z)$. If $I/I_0 = e^{-1}$, then $\alpha z = 1$. So, $z = 1/\alpha = 1/(2\,\mathrm{cm}^{-1}) = 0.5\,\mathrm{cm}$. This demonstrates that even at a very low vapor pressure (10^{-6} mbar), sodium exhibits **strong resonance absorption** for the D-lines, significantly attenuating light over a short path length. This underscores the large oscillator strength of this transition.

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We've covered a lot of ground in this section.

Slide 32:

summarizes the **Key Take-Aways from Section 2.7**.

* First, we've established how the **Microscopic picture** (involving Einstein coefficients A and B, oscillator strength f, and absorption cross section σ) and the **Macroscopic picture** (involving the absorption coefficient α and the imaginary part of refractive index κ) are **quantitatively linked**. We can derive macroscopic optical properties from fundamental atomic/molecular transition parameters.

* Second, **Integrated quantities like the line strength** S_{ik} (integral of $\sigma\, d\nu$) **and the averaged cross section** $\bar{\sigma}_{ik}$ are experimentally convenient. They provide robust measures of transition strength that can be extracted from experimental spectra, often more easily than determining the peak values or exact line shapes if broadening is complex.

* Third, the **Sum rule,** $\sum_k f_{ik} = 1$ (for a one-electron system, or normalized per electron), **ensures energy conservation across all transitions** originating from a given state. It means the total "absorption capability" of an electron is fixed and distributed among its possible transitions.

* Fourth, for a transition whose linewidth is determined solely by its natural lifetime (natural broadening), the **Natural linewidth uniquely fixes the peak**

averaged absorption cross section, $\bar{\sigma}_{ik}$, to be proportional to λ_{ik}^2 (e.g., $\frac{\lambda_{ik}^2}{4}$, under certain conditions), making it strikingly independent of the specific lifetime (or A_{ik} value) in that final formula. While the lifetime (via A_{ik}) determines the natural linewidth AND the integrated strength, these two dependencies cancel out when calculating the peak cross section for such an ideal, naturally broadened line. This results in the simple $\frac{\lambda^2}{4}$ type of formula.

These are the core concepts that provide the foundation for understanding how light interacts with atoms and molecules in the context of absorption and emission.

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To conclude this section:

- **These foundations underpin modern high-resolution laser spectroscopy.** The concepts of Einstein coefficients, cross sections, oscillator strengths, and the factors governing absorption and emission are absolutely essential for designing experiments, interpreting spectra, and extracting quantitative information about atomic and molecular systems.
- Furthermore, these concepts **will be crucial for interpreting Doppler and pressure broadening in Chapter 3.** Understanding the intrinsic properties of a spectral line, like its natural width and strength (which we've discussed here), is a prerequisite for understanding how these lines are modified by the environment of the atoms or molecules – such as their thermal motion (Doppler broadening) or collisions with other particles (pressure broadening).

So, please make sure you are comfortable with the material from Section 2.7, as we will be building directly upon it as we move forward. Thank you.