Vol. 2

Chapter 2.1

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Good morning, everyone. Welcome back to Physics 608, Laser Spectroscopy.

I'm Distinguished Professor Dr M A Gondal, and today, we begin a new and foundational topic, which I've designated as Chapter 2.1 in our course notes.

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The title of this chapter, and the core theme for our next few lectures, is **Linear and Nonlinear Absorption**. This distinction is absolutely central to understanding modern laser spectroscopy. In your undergraduate optics and quantum mechanics courses, you almost certainly dealt exclusively with linear absorption, governed by the familiar Beer-Lambert law. In that world, a material's ability to absorb light is a fixed property, independent of how bright the light is.

However, the advent of the laser, with its unprecedented intensity and monochromaticity, opened the door to a new regime of light-matter interactions—the nonlinear regime. Here, the material's response *changes* depending on the intensity of the incident light. The medium and the light field become deeply coupled in a way that gives rise to a host of new, powerful, and fascinating phenomena. Our goal today is to build a solid, quantitative foundation for understanding the simplest and most important of these: saturation absorption. This will be our gateway to the entire field of nonlinear spectroscopy.

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Alright, let's start with the motivation. Why do we even need to venture into the complexities of nonlinear spectroscopy? The answer lies in the pursuit of ever-higher resolution.

The first bullet point here states the primary objective: The goal of high-resolution spectroscopy is to resolve spectral features that are narrower than the Doppler width.

Let's unpack that. In any gas or vapor sample at a finite temperature, the atoms or molecules are not stationary. They are moving randomly, following a Maxwell-Boltzmann velocity distribution. Due to the Doppler effect, an atom moving towards the laser source sees the light blue-shifted, while an atom moving away sees it red-shifted. This means that even if every single atom has the exact same, infinitesimally sharp transition frequency in its own rest frame, the ensemble of atoms in the lab frame will absorb light over a broad range of frequencies. This broadening of the spectral line due to the thermal motion of the absorbers is called Doppler broadening, and its characteristic width is the Doppler width.

For many situations, especially in atomic and molecular physics, the Doppler width is the dominant broadening mechanism, often being hundreds of megahertz or even gigahertz wide. It acts like a thick curtain, obscuring the finer details of the energy level structure, such as hyperfine splittings or natural linewidths. To see those details, we must find a way to peek behind this Doppler curtain.

This is where our second point comes in. Single-mode, or narrow-band, lasers are the key. They provide two essential properties: incredibly high spectral brightness, meaning a lot of power in a very narrow frequency range, and tunability. These properties enable what we call Doppler-free methods—techniques specifically designed to eliminate the effects of Doppler broadening. And the most fundamental of these methods relies on the nonlinear phenomenon of saturation.

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So, how do we use a laser to achieve this? The key strategy is laid out in the first point on this slide. We drive the absorbing transition so strongly that the lower-state population is depleted. The term we use for this is that the transition becomes "saturated." This very act of depletion creates a nonlinear light-matter interaction.

Let's think about this intuitively. Absorption happens because there are more atoms in the lower energy state than in the upper one. An incident photon gets absorbed, promoting an atom to the upper state. In the linear regime, with weak light, the atom quickly relaxes back down, ready to absorb another photon. The lower state population is barely affected. But if we hit the sample with an incredibly intense, resonant laser beam, we are promoting atoms to the upper state much faster than they can relax back down. The result? We run out of atoms in the lower state to do the absorbing! The ground state becomes depleted, and the population difference between the two states shrinks.

This leads directly to the result mentioned in the second bullet point. The absorption coefficient, which we usually think of as a constant, now becomes intensity-dependent. Let's call it alpha of I, α (I) $\alpha(I)$. As you increase the intensity I I, you deplete the ground state, which reduces the absorption coefficient. The medium effectively becomes more transparent, or "bleached," by the intense light. This intensity-dependent absorption is the hallmark of nonlinearity. And as we will see, signals derived from this nonlinear interaction contain sub-Doppler information, as well as enabling other fascinating effects like multiphoton phenomena.

So, the topic for this set of slides, our agenda if you will, is to develop the fundamental physics, the key definitions, and the quantitative formulas we need to understand saturation and the spectroscopic tools that are built upon it. We're going to build this up from first principles.

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Alright, let's lay out a road-map for this lecture so you can see how the concepts will build on one another.

First, we'll start with a quick recap of linear absorption. We need to establish our baseline and define our notation clearly. This is the world of Beer's Law, which should be familiar territory.

Second, we'll dive into the core concept of saturation. We will explore the population dynamics in a simple two-level system. A crucial distinction we'll

make here is between "open" and "closed" systems, which has profound practical consequences for experiments.

Third, we will get quantitative. We will define and learn how to calculate the two most important parameters in this field: the saturation parameter, which is a dimensionless quantity given by the symbol capital S S, and the saturation intensity, I s I_s. The saturation intensity is a critical benchmark for any experiment.

Fourth, we will connect this population-based picture to the more microscopic, coherent picture of light-matter interactions. We will discuss the relation of saturation to the Rabi frequency, which we denote as capital Omega sub R R, Ω R Ω_R. This will also give us a chance to reinforce the concepts of homogeneous versus inhomogeneous broadening, which are essential for understanding whose spectral features we can resolve.

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Continuing with our road-map, once we have the theoretical framework in place, we will move to practical evaluation. Physics is, after all, an experimental science.

We'll work through some numerical examples for real-world systems, like molecular beams and atomic vapors. We'll examine the influence of practical parameters like the laser's own bandwidth, the rate of collisions in the sample, and the duration of the laser pulse if we're not using a continuous wave laser.

This will ground our theory in the reality of the lab.

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Let's begin by solidifying the key idea: the distinction between a linear and a nonlinear response.

First, linear optics. This is the regime of low light intensity. The defining characteristic, as stated in the first bullet point, is that the absorbed power is directly proportional to the incident power. If you double the intensity of your flashlight, the material absorbs twice as much power. This implies that the absorption coefficient, little α α, is a constant. It's an intrinsic property of the material at that frequency, independent of the light's intensity. This is the domain of Beer's Law.

Now for nonlinear optics. Here, we use intense fields, like those from a laser. The populations of the quantum states are no longer determined solely by the thermal equilibrium described by the Boltzmann distribution. The intense light field is strong enough to actively alter the populations itself. As we discussed, it can deplete the ground state and populate the excited state. Because the absorption coefficient depends directly on the population difference, this means α α is no longer a constant. It becomes a function of intensity, α (I) $\alpha(I)$. This is the fundamental departure from the linear world.

Within nonlinear optics, there are many different effects. For our purposes, we can group them into two main classes.

The first is saturation, which is the focus of today's lecture. Saturation is a single-photon driven process. It involves the laser changing the populations of the very same transition that it is being used to probe. A single photon is

absorbed, changing the state populations, which in turn affects the absorption of subsequent photons from the same beam.

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The second major class of nonlinearities involves multiphoton processes. This includes effects like two-photon absorption, Raman scattering, and so on. In these cases, the interaction involves the simultaneous absorption of two or more photons. For example, an atom can be excited from state A to state C by simultaneously absorbing two photons whose individual energies don't match any intermediate state, but whose sum of energies precisely matches the A-to-C transition energy. These are fascinating and powerful spectroscopic tools in their own right, but they are typically higher-order, weaker effects than saturation.

Therefore, our focus here will be on saturation. It is the simplest, most direct, and most ubiquitous nonlinear process you will encounter in laser spectroscopy. Mastering it is the first and most important step into the world of nonlinear optics.

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To build a quantitative model, we first need a mathematical description of our light field. For the majority of our analysis, we will use the simplest and most useful model: a monochromatic plane wave.

The first bullet point shows how we write the electric field. The equation is: Capital E E as a function of z z and t t equals E 0 E_0 times the cosine of the quantity ω t − k z $\omega t - kz$. That is,

E (z , t) = E 0 cos ⁡ (ω t − k z)

$$E(z,t) = E_0 \cos(\omega t - kz)$$

Let's break this down. On the next slide, we have the symbols and units.

E 0 E_0, pronounced 'E-naught' or 'E-sub-zero', is the peak electric-field amplitude. It represents the maximum strength of the electric field. Its units are Volts per meter, V m − 1 $\mathrm{V\,m^{-1}}$.

The Greek letter ω ω, omega, is the angular frequency of the wave. It tells us how rapidly the field oscillates in time at a fixed point in space. Its units are radians per second, r a d s − 1 $\mathrm{rad\,s^{-1}}$. Of course, it's related to the ordinary frequency v ν in Hertz by ω = 2 π v $\omega = 2\pi\nu$.

The letter k k is the wave number, or more precisely, the angular wave number. It tells us how rapidly the field oscillates in space at a fixed moment in time. It's related to the wavelength λ λ by k = 2 π / λ $k = 2\pi/\lambda$. For a wave propagating in vacuum, the wave number is equal to the angular frequency divided by the speed of light, k = ω / c $k = \omega/c$. Its units are radians per meter, or simply inverse meters, m − 1 $\mathrm{m^{-1}}$.

The argument of the cosine, ω t − k z $\omega t - kz$, is the phase of the wave. The form ω t − k z $\omega t - kz$ describes a wave propagating in the positive z z-direction.

Page 11: Continuing with our definitions for the plane wave model:

c is, of course, the speed of light in vacuum, with a value of approximately 2.9979 × 10 8 2.9979×10^8 meters per second.

Now, in the lab, we don't usually measure the electric field directly. We measure power or intensity. The intensity of a light wave is the power per unit area, typically in units of Watts per square meter. For an oscillating field, we are interested in the average intensity, averaged over one cycle of the oscillation. The relationship between this cycle-averaged intensity, capital I, and the peak electric field amplitude, E_0 , is given by the crucial formula:

Capital I equals 1 2 c ϵ 0 E 0 2 $1/2\, c\epsilon_0 E_0^2$.

That is, I = 1 2 c ϵ 0 E 0 2 .

$$I = \frac{1}{2} c \epsilon_0 E_0^2.$$

Here, ε_0 , epsilon-naught, is the permittivity of free space, a fundamental constant with the value 8.854 × 10 − 12 8.854×10^{-12} Farads per meter.

Notice the key relationship: the intensity, which is what our power meters measure, is proportional to the \textit{square} of the electric field amplitude. This is a general feature of electromagnetic waves. To double the intensity, you only need to increase the E-field amplitude by a factor of 2 $\sqrt{2}$.

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This slide provides a simple visual for the model we've just discussed. Here we see a snapshot of our monochromatic plane wave at a fixed moment in time, say t = 0 $t = 0$.

The plot shows the Electric field, capital E E, on the vertical axis, versus the propagation direction, z z, on the horizontal axis. As you can see, the field varies sinusoidally in space.

The diagram explicitly labels the key parameters. The peak amplitude of the wave, the maximum value the electric field reaches, is labeled E 0 E_0. This is the quantity we discussed, measured in Volts per meter.

The spatial period of the wave, the distance over which the wave pattern repeats itself, is the wavelength, labeled with the Greek letter λ λ, lambda. As we know, lambda is related to the wave number k k by λ = 2 π k $\lambda = \frac{2\pi}{k}$.

This simple, idealized wave is the light source we will use to interact with our atoms. It's a powerful model because any complex light field can be decomposed into a sum of such plane waves through Fourier analysis.

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Now that we have our model for the light, let's introduce the 'matter' side of the light-matter interaction. We'll consider a single transition within an atom or molecule.

The first point establishes the most fundamental condition for any spectroscopic interaction: the energy and frequency match. We have a transition from a lower energy level, E i E_i, to an upper energy level, E k E_k. For light to be absorbed, the energy of the photon must precisely match the energy difference between these two states. This is the Bohr frequency

condition, written here as: Capital Delta E E equals E k − E i $E_k - E_i$, which must equal $\hbar$ ω $\hbar\omega$.

Δ E = E k − E i = $\hbar$ ω

$$\Delta E = E_k - E_i = \hbar\omega$$

Here, $\hbar$ $\hbar$, or h-bar, is the reduced Planck constant, and ω ω is the angular frequency of our laser light. This equation is the heart of resonance. The laser is like a key, and the atomic transition is the lock. They only interact strongly if the key fits perfectly.

Let's define our symbols. We'll use Dirac notation, or bra-ket notation, as it's the language of quantum mechanics. The ket | i ⟩ $|i\rangle$ represents the quantum state of the lower level, which has energy E i E_i. The ket | k ⟩ $|k\rangle$ represents the quantum state of the upper level, which has energy E k E_k.

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Continuing with our definitions for the atomic system:

As mentioned, $\hbar$ $\hbar$ is the reduced Planck constant, with a value of 1.054 × 10 − 34 1.054×10^{-34} Joule-seconds. We assume our laser, with its angular frequency ω ω, is tuned to be resonant with this transition.

The next concept is the absorption cross section, denoted σ i k (ν) $\sigma_{ik}(\nu)$, pronounced sigma-sub-i-k of nu. This is a phenomenological but incredibly useful quantity. You can think of it as the "effective target area" that the absorbing particle presents to the incoming photons. If a photon "hits" this area, it gets absorbed. The larger the cross section, the more likely absorption is to occur. Crucially, it's a function of frequency, ν ν, meaning it

has a certain lineshape—it's largest on resonance and falls off as the laser is detuned. The unit of cross section is area, so in SI units, it's meters squared, m 2 m^2.

Finally, we come to a concept of paramount importance for both linear and nonlinear absorption: the population difference, which we'll denote capital Δ N ΔN. Net absorption of light is not just about having atoms in the ground state. It's about the *difference* between the number of atoms in the lower state and the upper state. The definition given here is: Capital Delta Δ N ΔN equals N i N_i minus the ratio g i / g k $g_\mathrm{i}/g_\mathrm{k}$ times N k N_k.

Δ N = N i − g i g k N k

$$\Delta N = N_\mathrm{i} - \frac{g_\mathrm{i}}{g_\mathrm{k}} N_\mathrm{k}$$

Here, N i N_i and N k N_k are the number densities (number of atoms per unit volume) in the lower and upper states, respectively. g i g_i and g k g_k are the statistical weights, or degeneracies, of the levels. They count how many distinct quantum states have the same energy E i E_i or E k E_k. The reason for this specific form, which accounts for both absorption from i i to k k and stimulated emission from k k down to i i, comes from a more detailed analysis using Einstein coefficients, which we will touch on later. For now, accept this as the effective population difference that drives net absorption. For a typical absorbing medium, N i N_i is much larger than N k N_k, so Δ N ΔN is positive.

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Now we are ready to combine our model of the light field with our model of the atomic medium to derive a fundamental relationship for power absorption. We'll perform an infinitesimal power balance calculation.

Let's set up the geometry. Imagine our laser beam, with a cross-sectional area A A (in meters squared), is traveling through our absorbing medium. The incident intensity is I 0 I_0, which is the incident power P 0 P_0 divided by the area A A.

Now, consider a very thin slice of this medium, with thickness d z dz, as the beam propagates through it. As the light passes through this slice, some of its power will be absorbed. We want to find the infinitesimal change in power, d P dP.

The central equation on this slide gives us the answer: d P dP equals minus A A times I 0 I_0 times σ i k (ν) $\sigma_{ik}(\nu)$ times Δ N ΔN times d z dz.

d P = − A I 0 σ i k (ν) Δ N d z

$$dP = -A\, I_0\, \sigma_{ik}(\nu)\, \Delta N\, dz$$

Let's take a moment to understand the physical meaning of every single factor in this equation. This is not just symbol pushing; there is clear physical logic here.

First, A A times d z dz. This is the area of our beam times the thickness of our slice. This product is simply the volume of the slice, d V dV.

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Let's continue deconstructing our power balance equation.

Next, I 0 I_0. As we defined it, this is the intensity, which can also be thought of as the photon flux density, representing energy per unit area per unit time.

Now, consider the product σ i k σ_{ik} times Δ N ΔN. σ i k σ_{ik} is the cross section per particle, and Δ N ΔN is the effective number density of absorbing particles. So this product, σ i k Δ N $\sigma_{ik}\,\Delta N$, represents the effective absorption area per unit volume of the medium. We often define this entire product as the absorption coefficient, α α. So

α = σ i k Δ N .

$$\alpha = \sigma_{ik}\,\Delta N.$$

Let's put it all together. The total number of effective absorbers in our slice is the number density Δ N ΔN times the volume of the slice, A d z $A\,dz$. The total absorbing area presented by these atoms is this number of atoms multiplied by the cross section per atom, σ i k σ_{ik}. So the total target area is

(A d z) × (Δ N σ i k) .

$$(A\,dz) \times (\Delta N\,\sigma_{ik}).$$

The amount of power absorbed is this total target area multiplied by the power per unit area, which is the intensity I 0 I_0. This gives us

I 0 × (A d z) × (Δ N σ i k) ,

$$I_0 \times (A\,dz) \times (\Delta N\,\sigma_{ik}),$$

which is exactly the expression we have, apart from the sign.

Finally, the negative sign. This is crucial. It signifies that power is being *removed* from the beam due to absorption. As the beam propagates in the positive z z direction, its power P P decreases. d P dP is a negative quantity.

So, this simple-looking differential equation is built on a solid, intuitive physical foundation.

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We can now use our infinitesimal power balance equation to derive the famous Beer's Law, which describes absorption in the linear regime.

The key assumption for linearity, as stated in the first point, is that we are using a weak incident intensity. "Weak" means that the rate of absorption is so low that it doesn't significantly alter the populations N i N_i and N k N_k. Therefore, the population difference Δ N ΔN remains constant, at its thermal equilibrium value. If Δ N ΔN is constant, and the cross section σ i k σ_{ik} is a property of the atom, then their product, the absorption coefficient α α, is also a constant.

So, α = σ i k Δ N = constant .

$$\alpha = \sigma_{ik}\,\Delta N = \text{constant}.$$

Now let's rewrite our infinitesimal form. The equation was d P = − A I 0 σ i k Δ N d z .

$$dP = -AI_0\,\sigma_{ik}\,\Delta N\,dz.$$

We can substitute I 0 = P / A $I_0 = P/A$ and α = σ i k Δ N $\alpha = \sigma_{ik}\,\Delta N$. This gives d P = − A (P A) α d z ,

$$dP = -A\left(\frac{P}{A}\right)\alpha\, dz,$$

and the areas A A cancel out, leading to the simple differential equation: d P d z = − α P .

$$\frac{dP}{dz} = -\alpha\, P.$$

This equation is one of the simplest and most common in physics. It states that the rate of change of power with distance is proportional to the power itself.

To find the power P (z) $P(z)$ after the beam has traveled a distance z z through the medium, we just need to integrate this equation. The solution is a simple exponential decay:

P (z) = P 0 exp ⁡ (− α z) .

$$P(z) = P_0 \exp(-\alpha z).$$

This is the Beer-Lambert Law. It says that the power of a light beam decreases exponentially as it propagates through a linear absorbing medium. P 0 P_0 is the initial power at z = 0 $z = 0$, and α α is the absorption coefficient that characterizes how strongly the medium absorbs the light.

Page 19: Let's add a couple of final notes on Beer's Law

The product α z αz in the exponent is often given its own name: the optical depth, denoted by the Greek letter τ τ (tau). So, τ = α z $\tau = \alpha z$. The optical depth is a dimensionless measure of how opaque a medium is. If τ τ is much less than 1, the medium is optically thin, and not much light is absorbed. If τ τ is much greater than 1, the medium is optically thick, and most of the light is absorbed. In this notation, Beer's law becomes P (z) = P 0 exp ⁡ (− τ) $P(z) = P_0 \exp(-\tau)$.

The second point on this slide is the most important one to remember. Beer's Law, and the entire concept of a constant absorption coefficient, is valid *only* when α α is independent of the incident intensity I 0 I_0. This is the definition of the linear regime. As soon as α α starts to depend on I 0 I_0, we enter the nonlinear world, and Beer's Law breaks down. This is precisely the territory we are heading into.

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This graph provides an excellent visualization of Beer's Law. The title says it all: "Beer's Law: Exponential Attenuation (Semi-Log Plot)".

Let's analyze the axes. The horizontal axis is the path length z z through the medium, in arbitrary units. The vertical axis is the transmitted power P (z) $P(z)$, also in arbitrary units, but it's plotted on a logarithmic scale. This is what "semi-log plot" means.

The equation for the line is given right on the graph: P (z) = P 0 exp ⁡ (− α z) $P(z) = P_0 \exp(-\alpha z)$. If we take the natural logarithm of both sides of this equation, we get:

ln ⁡ (P (z)) = ln ⁡ (P 0) − α z .

$$\ln\big(P(z)\big) = \ln(P_0) - \alpha z.$$

This is the equation of a straight line. If we plot ln ⁡ (P) $\ln(P)$ on the y-axis and z z on the x-axis, the y-intercept is ln ⁡ (P 0) $\ln(P_0)$ and the slope is − α $-\alpha$. Because our vertical axis is logarithmic, the exponential decay function appears as a straight line.

We can see this on the plot. At z = 0 $z = 0$, the power is P 0 P_0, which is normalized to 1 on this graph. As z z increases, the power drops. The fact that the blue line is perfectly straight confirms the exponential nature of the decay. And as labeled, the slope of this line is equal to the negative of the absorption coefficient, − α $-\alpha$.

The dashed red lines illustrate this. For a certain change in path length, Δ z Δz, there is a corresponding change in the logarithm of the power, Δ (ln ⁡ P) $\Delta(\ln P)$. The ratio, Δ (ln ⁡ P) / Δ z $\Delta(\ln P)/\Delta z$, gives the slope, − α $-\alpha$. This is a very common way to measure absorption coefficients in the lab. You measure the transmitted power for several different path lengths, plot the data on a semi-log graph, and fit a straight line to it. The slope gives you your answer.

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So, how do we experimentally observe the transition from the linear regime to the nonlinear, saturated regime? One of the most convenient methods is by monitoring fluorescence.

The first point explains the principle. When an atom or molecule absorbs a photon and goes to the upper state, which we've labeled | k ⟩ $|k\rangle$, it has to relax back down. One common relaxation pathway is radiative decay, or fluorescence, where it emits a photon. This emitted fluorescence light can be collected by a detector. The key insight is that the total fluorescence intensity, which we'll call I F L I_{FL}, is directly proportional to the rate at which atoms are being excited to the upper state. And that rate is, in turn, proportional to the power being absorbed by the sample. So, I F L I_{FL} is proportional to the absorbed power.

This gives us a powerful diagnostic tool. In the linear region, where absorbed power is proportional to incident intensity I 0 I_0, the fluorescence signal I F L I_{FL} will also increase linearly with I 0 I_0. If you double your laser intensity, you get double the fluorescence signal.

However, as we increase the incident intensity I 0 I_0 further, we start to deplete the ground state. The populations begin to saturate. Since the medium becomes less absorbing, the absorbed power no longer increases linearly with I 0 I_0. The curve of absorbed power versus incident intensity starts to bend and eventually levels off. Because the fluorescence just mirrors the absorbed power, the curve of I F L I_{FL} versus I 0 I_0 will show the exact same behavior.

The great advantage of this technique, as noted in the final bullet point, is that it's a "background-free" measurement. You shine your laser in, and

you collect the fluorescence photons, which are typically emitted in all directions, at a right angle to the laser beam. In this geometry, you're not trying to measure a small change in a very large transmitted laser power, which can be difficult. Instead, you're measuring an emitted signal against a nearly dark background. This makes it a very sensitive way to detect absorption and observe the onset of saturation.

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This figure, titled "Monitoring Absorption via Fluorescence Saturation," illustrates exactly the behavior we just discussed.

Let's look at the axes. The horizontal axis is the incident laser intensity, I 0 I_0. The vertical axis is the measured fluorescence intensity, I F L I_{FL}.

At very low incident intensities, close to the origin, you can see a dashed line labeled "Linear Region." Here, the blue curve representing our signal is essentially a straight line. The fluorescence is directly proportional to the incident intensity. This is the Beer's Law regime.

As we crank up the laser intensity, moving to the right along the horizontal axis, the blue curve clearly starts to bend over. The slope decreases. This region is marked with an arrow labeled "Saturation Onset (Knee)". This is the "knee" of the curve, where the nonlinearity becomes significant. We are no longer getting a proportional increase in fluorescence for an increase in laser power. We are starting to saturate the transition.

Finally, at very high incident intensities, the curve becomes almost horizontal, approaching a "Plateau." In this regime, we are in deep saturation. We are exciting atoms to the upper state as fast as they can

possibly be excited, limited by their relaxation rates. The absorbed power has leveled off, and therefore, so has the fluorescence. Pumping the system with even more laser power yields diminishing returns; the fluorescence signal barely increases.

This saturation curve is the characteristic signature of this nonlinear process, and measuring it is a standard technique in any laser spectroscopy lab.

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Let's formalize what's happening beyond the linear regime. The key is that the absorption coefficient, α α, is now dependent on intensity.

The first point gets to the heart of the physics: there's a competition. On one hand, we have the absorption rate, which is driven by the laser and is proportional to the incident intensity I 0 I_0. On the other hand, we have the various relaxation processes (spontaneous emission, collisions, etc.) that try to return the system to thermal equilibrium. When the absorption rate becomes comparable to the relaxation rate, the population of the lower state, N i N_i, begins to diminish significantly.

This means we have to generalize our differential law for absorption. Instead of d P = − P α d z $dP = -P\,\alpha\,dz$, where α α is a constant, we must now write:

d P = − P 0 α (I 0) d z .

$$dP = -P_0\,\alpha(I_0)\,dz.$$

Or, more fundamentally,

d P = − P 0 σ i k Δ N (I 0) d z .

$$\mathrm{d}P = -P_0\,\sigma_{ik}\,\Delta N(I_0)\,\mathrm{d}z.$$

The crucial change is that both the absorption coefficient α α and the population difference Δ N ΔN are now functions of the incident intensity I 0 I_0.

As you increase I 0 I_0, Δ N ΔN decreases because you're moving population from the lower to the upper state. Consequently, α (I 0) $\alpha(I_0)$ also decreases. It's a monotonically decreasing function of I 0 I_0.

This phenomenon goes by several names, which are standard terminology you should be familiar with. It's called "nonlinear absorption," for obvious reasons. It's often called "saturation absorption," which is the term we'll favor. And a very descriptive term is "bleaching." The medium is "bleached" by the light, meaning it becomes more transparent. Just like bleaching a colored cloth makes it lose its color (its ability to absorb certain wavelengths), intense resonant light makes the medium lose some of its ability to absorb that light.

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To make the idea of an intensity-dependent absorption coefficient more concrete, let’s look at a simple algebraic example. This is a phenomenological model, a “toy model” if you will, but it’s very instructive.

Let’s imagine that for small intensities, we can approximate the behavior of α (I) $\alpha(I)$ using a first-order Taylor expansion around I = 0 $I = 0$. This gives us the model shown:

α (I) = α 0 (1 − b I) .

$$\alpha(I) = \alpha_0(1 - b\,I).$$

Let’s define the terms here.

α 0 α_0, or alpha-naught, is the small-signal absorption coefficient. This is the familiar, constant absorption coefficient from Beer's Law that you’d measure in the limit of very low intensity.

b b is an empirical constant that characterizes the strength of the nonlinearity. Its units must be inverse intensity, for instance, square meters per Watt (m 2 W − 1 $\mathrm{m}^2\,\mathrm{W}^{-1}$), to make the term b I bI dimensionless.

Now, let’s substitute this simple nonlinear model for α α into our power balance equation.

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Substituting our model α (I) = α 0 (1 − b I) $\alpha(I) = \alpha_0(1 - bI)$ into the power balance equation d P = − A I α (I) d z $\mathrm{d}P = -A\,I\,\alpha(I)\,\mathrm{d}z$ gives us the following expression:

d P = − A (I α 0 − α 0 b I 2) d z .

$$\mathrm{d}P = -A(I\alpha_0 - \alpha_0 bI^2)\,\mathrm{d}z.$$

Let's examine the terms inside the parentheses. The first term, I α 0 $I\alpha_0$, is linear in intensity I I. This is the familiar term that leads to Beer's Law. The second term, − α 0 b I 2 $-\alpha_0 bI^2$, is quadratic in intensity, proportional to I I squared. This is the new, nonlinear term that arises from our model.

We don't need to solve this differential equation right now; the slide notes that the solution involves logarithmic and inverse power terms.

The key conceptual point is to see how even the simplest possible model of nonlinearity—a linear decrease in α α with I I—introduces higher-order terms in intensity into the fundamental equation for power absorption. This demonstrates conceptually how the behavior deviates from the simple exponential decay of Beer's Law.

Page 26: Now, we need to address a very important and practical point: the relationship between the laser's spectral width and the transition's width.

Now, we need to address a very important and practical point: the relationship between the laser's spectral width and the transition's width. So far, we've been a bit cavalier, assuming a perfectly monochromatic laser and a perfectly sharp transition. In reality, both have finite spectral widths, and their interaction depends on their overlap.

First, let's define spectral intensity density. We can't just talk about the total intensity I I anymore. We need to know how that intensity is distributed over different frequencies. We define ρ ν (ν) $\rho_\nu(\nu)$ (rho-sub-nu of nu) as the spectral energy density, which is energy per unit volume per unit

frequency interval. This is related to the spectral intensity density, I v (v) $I_\nu(\nu)$ (I-sub-nu of nu), by a factor of the speed of light: ρ v (v) = I v (v) / c $\rho_\nu(\nu) = I_\nu(\nu)/c$. I v I_ν has units of Watts per square meter per Hertz.

The total intensity, I I, is then the integral of the spectral intensity I v I_ν over all frequencies. For a laser with a finite bandwidth, δ v L $\delta\nu_\mathrm{L}$ (delta-nu-sub-L), we can approximate this integral, as shown in the equation:

I = ∫ I v (v) d v ≈ I v (v 0) δ v L .

$$I = \int I_\nu(\nu)\, d\nu \approx I_\nu(\nu_0)\, \delta\nu_\mathrm{L}.$$

Here, v 0 ν_0 is the center frequency of the laser. This approximation assumes that the laser has a roughly flat-top spectrum across its bandwidth, which is often a reasonable starting point.

This brings us to the most important distinction on this page.

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Here is the critical distinction we must always keep in mind when designing or analyzing an experiment.

First, there is the laser bandwidth, which we denote δ v L $\delta\nu_\mathrm{L}$. This is the frequency spread of the light source itself. A single-mode laser might have a bandwidth of a megahertz or less, while a multimode diode laser could have a bandwidth of many gigahertz.

Second, there is the absorption linewidth, which we denote δ v a $\delta\nu_\mathrm{a}$. This is the frequency range over which the atomic or molecular sample can absorb light. This linewidth can have contributions from both homogeneous

broadening (like natural lifetime broadening or collision broadening, which affects all absorbers equally) and inhomogeneous broadening (like Doppler broadening, where different absorbers have different resonant frequencies).

The total absorbed power, and indeed the entire nature of the saturation, depends critically on the spectral overlap of these two profiles: the laser's emission profile and the sample's absorption profile. We will now consider the consequences of this overlap.

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Let's write down the general expression for absorbed power, which explicitly accounts for these spectral profiles.

In a small volume element d V = A d z $dV = A\,dz$, the total absorbed power, which we'll now call Δ P ΔP to avoid confusion with the differential d P dP, is given by the overlap integral:

Capital Delta P equals Δ N d V $\Delta N\,dV$ times the integral of I v (v) σ i k (v) d v $I_\nu(\nu)\,\sigma_{ik}(\nu)\,d\nu$.

Δ P = Δ N d V ∫ I v (v) σ i k (v) d v

$$\Delta P = \Delta N\,dV \int I_\nu(\nu)\,\sigma_{ik}(\nu)\,d\nu$$

This equation is the most general statement. It says that for each little slice of frequency d v $d\nu$, the absorbed power is proportional to the intensity in that slice, I v (v) $I_\nu(\nu)$, and the absorption cross-section at that frequency, σ i k (v) $\sigma_{ik}(\nu)$. We then integrate over all frequencies to get the total absorbed power.

Now, let's look at two important special situations that simplify this integral.

Case 1: The laser is narrow and tuned to the peak of the transition. "Narrow" means the laser bandwidth δ v L $\delta\nu_L$ is much, much smaller than the absorption linewidth δ v a $\delta\nu_a$. In this case, the laser's spectrum I v (v) $I_\nu(\nu)$ is essentially a spike, a delta function, centered at the resonance frequency v 0 ν_0. The absorption cross section σ i k (v) $\sigma_{ik}(\nu)$ is broad and slowly varying over the laser's width. So, we can pull the constant value σ i k (v 0) $\sigma_{ik}(\nu_0)$ out of the integral. The remaining integral, ∫ I v (v) d v $\int I_\nu(\nu)\,d\nu$, is just the total intensity I I. The expression simplifies to:

Δ P ΔP equals Δ N d V $\Delta N\,dV$ times I (v 0) $I(\nu_0)$ times σ i k (v 0) $\sigma_{ik}(\nu_0)$.

Note a slight typo on the slide, it should really be the total intensity I I, not I (v 0) $I(\nu_0)$. So,

Δ P = Δ N d V I σ i k (v 0)

$$\Delta P = \Delta N\,dV\,I\,\sigma_{ik}(\nu_0)$$

Case 2: The laser is much broader than the absorption line. Here, δ v L $\delta\nu_L$ is much greater than δ v a $\delta\nu_a$.

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Continuing with Case 2, where the laser is much broader than the absorption line.

In this scenario, the atomic absorption profile σ i k (v) $\sigma_{ik}(\nu)$ is the narrow feature, looking like a spike, while the laser's spectral intensity I v (v)

$I_\nu(\nu)$ is broad and nearly constant over the absorption line. So this time, we can pull the constant value of the spectral intensity, I v (v 0) $I_\nu(\nu_0)$, out of the integral. The remaining integral, ∫ σ i k (v) d v $\int \sigma_{ik}(\nu)\, d\nu$, is the total integrated cross section.

A simpler, more intuitive way to think about this is that only the fraction of the laser's power that falls within the absorption linewidth can actually be absorbed. If the laser has a total intensity I I distributed over a bandwidth δ v L $\delta\nu_\mathrm{L}$, then the intensity per unit frequency is roughly I / δ v L $I/\delta\nu_\mathrm{L}$. The amount of this intensity that overlaps with the absorption line of width δ v a $\delta\nu_\mathrm{a}$ is then (I / δ v L) × δ v a $(I/\delta\nu_\mathrm{L}) \times \delta\nu_\mathrm{a}$.

So, we can say that only an effective fraction of the laser's intensity, given by the ratio δ v a / δ v L $\delta\nu_\mathrm{a}/\delta\nu_\mathrm{L}$, is available for absorption. The resulting absorbed power is: Δ P ΔP equals Δ N d V $\Delta N\, dV$ times I (v 0) $I(\nu_0)$ times σ i k (v 0) $\sigma_{ik}(\nu_0)$ times the fraction δ v a / δ v L $\delta\nu_\mathrm{a}/\delta\nu_\mathrm{L}$.

This tells us that if you use a broadband laser, much of its power is "wasted" because it's at the wrong frequency to be absorbed. This highlights the importance of what we call spectral brightness—power per unit bandwidth—which is a key figure of merit for lasers in spectroscopy.

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We've been using the phenomenological absorption cross-section, σ i k σ_{ik}. Now, let's connect this to the more fundamental parameters of quantum mechanics, specifically the Einstein coefficients. This link provides a deeper theoretical foundation for our model.

In 1917, Albert Einstein introduced his famous A and B coefficients to describe absorption, stimulated emission, and spontaneous emission. The rate of photon absorption can be expressed using the Einstein B coefficient for absorption, B i k B_{ik}.

The equation on the slide states that n ph n_{ph}, the number of photons absorbed per unit time in a volume d V dV, is given by:

n ph = B i k ρ v (v 0) Δ N d V

$$n_{\text{ph}} = B_{ik}\, \rho_{\nu}(\nu_0)\, \Delta N\, dV$$

Let's define these terms again for clarity:

n ph n_{ph} is the number of photons absorbed per second.

ρ v ρ_{ν}, rho-sub-nu, is the spectral energy density of the radiation field at the transition frequency, v 0 ν_0. Its units are Joules per cubic meter per Hertz (J m − 3 H z − 1 $J\,m^{-3}\,Hz^{-1}$). Remember, this is related to the spectral intensity I v I_{ν} by ρ v = I v / c $\rho_{\nu} = I_{\nu}/c$.

Δ N ΔN is our familiar effective population density difference, and d V dV is the volume element.

B i k B_{ik} is the Einstein coefficient for stimulated absorption, which is a fundamental constant for a given transition, encapsulating the quantum mechanical transition probability.

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Now we can make the connection. We have two different expressions for the rate of energy absorption.

From the previous discussion, the absorbed power Δ P ΔP for a narrow laser is Δ P = I σ i k Δ N d V $\Delta P = I\sigma_{ik}\Delta N\, dV$. The number of photons absorbed per second, n p h n_{ph}, is simply the absorbed power divided by the energy of a single photon, h v $h\nu$. So, n p h = Δ P h v = I σ i k Δ N d V h v $n_{\mathrm{ph}} = \frac{\Delta P}{h\nu} = \frac{I\sigma_{ik}\Delta N\, dV}{h\nu}$.

We also have the Einstein rate equation from the previous slide: n p h = B i k ρ v Δ N d V $n_{\mathrm{ph}} = B_{ik}\rho_\nu \Delta N\, dV$.

Let's equate these two expressions for n p h n_{ph}: I σ i k Δ N d V h v = B i k ρ v Δ N d V .

$$\frac{I\sigma_{ik}\Delta N\, dV}{h\nu} = B_{ik}\rho_\nu \Delta N\, dV.$$

We can cancel Δ N ΔN and d V dV from both sides. We also know the relationship between intensity I I and energy density ρ v ρ_ν. For a narrow laser, I = c ρ v $I = c\rho_\nu$. Substituting this in, we get: c ρ v σ i k h v = B i k ρ v .

$$\frac{c\rho_\nu\sigma_{ik}}{h\nu} = B_{ik}\rho_\nu.$$

The energy density ρ v ρ_ν cancels out, and we are left with a relationship between B i k B_{ik} and σ i k σ_{ik}.

The slide actually does this for the more general case involving the integrated cross section, which is the proper way. If you equate the general expressions, you find the beautiful and profound relation shown in the middle of the slide:

B i k B_{ik} equals c c over h v $h\nu$, times the integral from zero to infinity of σ i k (v) d v $\sigma_{ik}(\nu)\,d\nu$.

B i k = c h v ∫ 0 ∞ σ i k (v) d v .

$$B_{ik} = \frac{c}{h\nu}\int_0^{\infty} \sigma_{ik}\,(\nu)\,d\nu.$$

This is a powerful result. It shows that the fundamental quantum-mechanical transition probability, B i k B_{ik}, is directly proportional to the total integrated area under the absorption cross-section curve. The cross-section σ i k (v) $\sigma_{ik}(\nu)$ describes the lineshape of the transition, while B i k B_{ik} describes its total, intrinsic strength. This equation connects the two.

Page 32: The Integrated Absorption Cross-Section

This diagram provides a perfect visual summary of the relationship we just derived.

On the axes, we have the absorption cross-section, σ i k (v) $\sigma_{ik}(\nu)$, plotted on the vertical axis against the frequency, v ν, on the horizontal axis. The curve shows a typical absorption line profile, peaked at the resonant frequency v 0 ν_0. It could be a Gaussian profile from Doppler broadening, or a Lorentzian from lifetime broadening, or something more complex.

The blue bars represent a histogram, perhaps from a measurement, while the dashed red line is the theoretical lineshape function that fits the data.

The key takeaway is illustrated by the annotation. The Einstein B coefficient, B i k B_{ik}, is proportional to the total area under this curve. This area is the integrated cross-section, ∫ σ i k (ν) d ν $\int \sigma_{ik}(\nu)\, d\nu$. So, a "strong" transition, one with a large B i k B_{ik}, will have a large area under its absorption profile. This could mean it's a very tall and narrow peak, or a shorter but very broad peak. The total strength is determined by the total area. This provides a beautiful and intuitive link between a microscopic quantum property (B i k B_{ik}) and a macroscopically measurable quantity (the absorption lineshape and its area).

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We are now going to refine our model of the atomic system to make it more realistic. The simple two-level atom is a great starting point, but real systems are rarely so clean. We need to introduce the concept of an **open two-level system**.

First, what levels do we consider explicitly? We still focus on our two primary levels: a lower level, which from now on we'll label | 1 ⟩ $|1\rangle$, and an upper level, | 2 ⟩ $|2\rangle$. This is the transition we are probing with our laser.

The key feature of an "open" system is that there are additional "reservoir" levels that exist outside of our two-level model. Population can leak out from levels | 1 ⟩ $|1\rangle$ and | 2 ⟩ $|2\rangle$ into this reservoir, and population can also be replenished from the reservoir. What could these reservoir levels be? They could be other electronic or vibrational states, magnetic

sublevels, or simply represent the atom or molecule physically leaving the interaction region of the laser beam.

Therefore, as the third point states, the system is "open." This is in stark contrast to an idealized "closed" two-level atom, where the total population N 1 + N 2 $N_1 + N_2$ is strictly conserved. In an open system, the total population in our two levels of interest can change over time.

To model this mathematically, we will use rate equations. These equations must incorporate all the relevant physical processes: the laser-induced transitions (absorption and stimulated emission), spontaneous decay from level 2 to level 1, collisional relaxation processes that can move population around, and even molecular diffusion or transit-time effects, where molecules physically enter and leave the laser beam.

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This slide simply contains a descriptive caption for the diagram we're about to see on the next page. It summarizes the key concepts of an open two-level system.

It reiterates that unlike an idealized closed system, an open system accounts for interactions with its environment.

It consists of the two primary levels, | 1 ⟩ |1⟩ and | 2 ⟩ |2⟩. Population can leak to or be replenished from a "reservoir" of other states.

The diagram will show the key processes: laser-induced transitions, spontaneous decay, and these crucial relaxation and replenishment pathways to and from the reservoir.

Let’s look at the diagram itself.

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Here is the energy level diagram for our open two-level system. This is a critically important picture to have in your mind.

On the vertical axis, we have energy. We see two discrete energy levels, the lower state | 1 ⟩ $|1\rangle$ and the upper state | 2 ⟩ $|2\rangle$.

Let's look at the processes connecting these two levels. The wavy red arrow pointing up from | 1 ⟩ $|1\rangle$ to | 2 ⟩ $|2\rangle$ represents laser-induced absorption. The wavy red arrow pointing down from | 2 ⟩ $|2\rangle$ to | 1 ⟩ $|1\rangle$ represents stimulated emission. Both are driven by the laser field, and they are collectively labeled W i n d W_{ind}, for the induced transition rate. The wavy blue arrow from | 2 ⟩ $|2\rangle$ to | 1 ⟩ $|1\rangle$ represents spontaneous emission, with its characteristic rate A 21 A_{21}. This happens even without a laser field present.

Now for the "open" part. To the right, we have a box labeled "Reservoir Levels." This represents all other states in the universe besides | 1 ⟩ $|1\rangle$ and | 2 ⟩ $|2\rangle$. There are dashed green arrows showing the coupling. There is an outflow rate from level | 2 ⟩ $|2\rangle$ to the reservoir, labeled Γ o u t Γ_{out} (capital Gamma out). This could be decay to some other third level, or collisional de-excitation. There is also an inflow rate from the reservoir to level | 1 ⟩ $|1\rangle$, labeled Γ i n Γ_{in} (capital Gamma in). This could represent molecules in the ground state diffusing into the laser beam, or collisional processes populating level | 1 ⟩ $|1\rangle$. There could also be other rates, like

outflow from | 1 ⟩ $|1\rangle$ or inflow to | 2 ⟩ $|2\rangle$, but these are the most common ones to consider.

This diagram encapsulates all the population traffic we need to account for in our mathematical model.

Page 36:

Now, let's translate the physical picture from the previous slide into a set of mathematical equations. These are the famous **rate equations**.

For simplicity, we'll start with the case of non-degenerate levels, meaning the statistical weights are g 1 = g 2 = 1 $g_1 = g_2 = 1$. This simplifies the Einstein coefficients, since B 12 = B 21 $B_{12} = B_{21}$.

We have two coupled, first-order ordinary differential equations, one for the population of each level.

The first equation describes the rate of change of the population density in the lower level, N 1 N_1:

d N 1 d t = B 12 ρ v (N 2 − N 1) − R 1 N 1 + C 1

$$\frac{dN_1}{dt} = B_{12}\,\rho_\nu\,(N_2 - N_1) - R_1\,N_1 + C_1$$

Let's break this down term by term.

The term B 12 ρ v (N 2 − N 1) $B_{12}\,\rho_\nu\,(N_2 - N_1)$ describes the change in N 1 N_1 due to the laser field. B 12 ρ v N 2 $B_{12}\,\rho_\nu\,N_2$ represents molecules arriving in level 1 via stimulated emission from level 2. B 12 ρ v N 1

$B_{12}\,\rho_\nu\,N_1$ represents molecules leaving level 1 via absorption. The net effect is proportional to N 2 − N 1 $N_2 - N_1$.

The term − R 1 N 1 $-R_1\,N_1$ represents all processes that cause population to *leave* level 1, at a total rate R 1 R_1. This could be diffusion out of the beam, for example.

The term + C 1 $+C_1$ represents all processes that cause population to *enter* level 1 from outside, at a constant rate C 1 C_1. This could be diffusion into the beam.

The second equation describes the rate of change of the population density in the upper level, N 2 N_2:

d N 2 d t = B 12 ρ v (N 1 − N 2) − R 2 N 2 + C 2

$$\frac{dN_2}{dt} = B_{12}\,\rho_\nu\,(N_1 - N_2) - R_2\,N_2 + C_2$$

This has a similar structure.

The term B 12 ρ v (N 1 − N 2) $B_{12}\,\rho_\nu\,(N_1 - N_2)$ is the change due to the laser. It's exactly the negative of the corresponding term for N 1 N_1, since a molecule that leaves level 1 via absorption must arrive in level 2.

The term − R 2 N 2 $-R_2\,N_2$ is the total depopulation rate of the upper level. This is a very important term; it includes spontaneous emission (A 21 A_{21}), collisional quenching, and any other decay out of level 2.

The term + C 2 $+C_2$ is an external pumping rate that might populate level 2 directly. In many cases, this is zero.

These two equations form the mathematical core of our model for saturation in an open system.

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Let's clearly define the terms we've introduced in the rate equations.

1. R i N i $R_i N_i$: This product represents the total depopulation rate of level i i. So R i R_i is the total rate constant for leaving level i i, with units of inverse seconds. It's a sum of all possible loss channels. For the upper state, R 2 R_2 would include the spontaneous emission rate A 21 A_{21}, plus a rate for collisions, plus a rate for transit out of the beam, and so on.

R 2 = A 21 + R c o l l i s i o n a l + R t r a n s i t + ...

$$R_2 = A_{21} + R_{\text{collisional}} + R_{\text{transit}} + \cdots$$

For the ground state, R 1 R_1 would typically be dominated by the transit rate.

2. C i C_i: This is the inflow rate into level i i from all external channels. It's a pumping term, representing how quickly population is supplied to our two-level system from the outside world. Units would be number of atoms per cubic meter per second. For example, in a molecular beam experiment, C 1 C_1 would represent the rate at which fresh ground-state molecules enter the laser interaction volume.

3. The third point is a reminder of a detail we've already used. In the case of non-degenerate levels (g 1 = g 2 = 1 $g_1 = g_2 = 1$), the Einstein coefficients for stimulated absorption and stimulated emission are equal: B 12 = B 21 $B_{12} = B_{21}$. This is why the same coefficient B 12 B_{12} appears in

both rate equations, simplifying the analysis. If the levels were degenerate, we would have g 1 B 12 = g 2 B 21 $g_1 B_{12} = g_2 B_{21}$.

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Before we analyze the full system with the laser on, it's essential to establish a baseline. What do the populations look like in the absence of the laser? This gives us the unsaturated populations.

To find this, we take our rate equations and set the laser intensity to zero. This means the spectral energy density ρ ν ρ_ν is zero. All the terms with B 12 B_{12} vanish. We are also interested in the stationary, or steady-state, solution, which means the populations are no longer changing in time. So, we set d N 1 d t $\frac{dN_1}{dt}$ and d N 2 d t $\frac{dN_2}{dt}$ to zero.

The rate equations become simple algebraic equations:

0 = − R 1 N 1 0 + C 1

$$0 = -R_1 N_1^0 + C_1$$

0 = − R 2 N 2 0 + C 2

$$0 = -R_2 N_2^0 + C_2$$

The superscript '0' indicates that these are the unsaturated, laser-off populations. Solving these is trivial. We find N 1 0 = C 1 / R 1 $N_1^0 = C_1/R_1$ and N 2 0 = C 2 / R 2 $N_2^0 = C_2/R_2$.

The slide shows the solution for the unsaturated population *difference*, Δ N 0 ΔN^0. The slide defines Δ N ΔN as N 2 − N 1 $N_2 - N_1$, so:

Δ N 0 = N 2 0 − N 1 0 = C 2 R 2 − C 1 R 1

$$\Delta N^0 = N_2^0 - N_1^0 = \frac{C_2}{R_2} - \frac{C_1}{R_1}$$

Combining the fractions gives the expression shown:

Δ N 0 = C 2 R 1 − C 1 R 2 R 1 R 2

$$\Delta N^0 = \frac{C_2 R_1 - C_1 R_2}{R_1 R_2}$$

Now, for a typical absorbing transition, the ground state population N 1 0 N_1^0 is much larger than the upper state population N 2 0 N_2^0. This means that our population difference Δ N = N 2 − N 1 $\Delta N = N_2 - N_1$ will be a negative number. This is important to keep track of. The slide notes Δ N 0 < 0 $\Delta N^0 < 0$ for an absorbing transition. Some textbooks define Δ N ΔN as N 1 − N 2 $N_1 - N_2$ to keep it positive. It doesn't matter as long as you are consistent. We will stick with the slide's convention.

This unsaturated population difference Δ N 0 ΔN^0 is our crucial reference point. The degree of saturation will be defined by how much the laser reduces the population difference relative to this initial value.

Page 39:

Now for the main event: let's find the stationary solution with the laser turned on. We are still in steady-state, so d N / d t dN/dt is zero, but now the energy density ρ v ρ_ν is not zero. We need to solve the full system of coupled algebraic equations. I will spare you the algebra, which is

straightforward but a bit tedious, and jump straight to the beautiful and very important result.

The steady-state population difference with the laser on, Δ N ΔN, is related to the unsaturated population difference Δ N 0 ΔN^0 by the following formula:

Δ N = Δ N 0 1 + B 12 ρ v (1 R 1 + 1 R 2) .

$$\Delta N = \frac{\Delta N^0}{1 + B_{12}\,\rho_\nu \left(\frac{1}{R_1} + \frac{1}{R_2}\right)}.$$

Look at this structure. The laser's effect is entirely contained in that second term in the denominator. If the laser is off (ρ v = 0 $\rho_\nu = 0$), the denominator is 1, and we get Δ N = Δ N 0 $\Delta N = \Delta N^0$, as expected. As the laser intensity ρ v ρ_ν increases, the denominator gets larger, and the magnitude of the population difference | Δ N | $|\Delta N|$ gets smaller. The transition is being saturated.

To make this expression even more elegant and physically transparent, we introduce a new quantity: the dimensionless saturation parameter, capital S S. The result can then be written as:

Δ N = Δ N 0 1 + S .

$$\Delta N = \frac{\Delta N^0}{1 + S}.$$

By comparing the two forms, we can see the definition of S S:

S = B 12 ρ v R ∗ .

$$S = \frac{B_{12}\,\rho_\nu}{R^*}.$$

Where R ∗ R^* is a newly defined effective relaxation rate, given by:

R ∗ = R 1 R 2 R 1 + R 2 .

$$R^* = \frac{R_1\,R_2}{R_1 + R_2}.$$

This parameter S S is the single most important quantity for describing saturation. It is a dimensionless number that tells you exactly how saturated your transition is.

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Just a quick note on the mathematical nature of the effective relaxation rate R ∗ R^* that we just defined.

The slide points out that R ∗ R^* is the harmonic mean of the two relaxation rates, R 1 R_1 and R 2 R_2.

Remember, the arithmetic mean is R 1 + R 2 2 $\frac{R_1+R_2}{2}$. The geometric mean is R 1 R 2 $\sqrt{R_1\,R_2}$. And the harmonic mean is the reciprocal of the arithmetic mean of the reciprocals, which is 1 (1 R 1 + 1 R 2) / 2 .

$$\frac{1}{\left(\frac{1}{R_1} + \frac{1}{R_2}\right)/2}.$$

Our \(R^\) *is off by a factor of 2 from this standard definition, but it arises naturally from the algebra of the rate equations and represents the characteristic rate that governs the saturation process in an open system.*

It's dominated by the slower* of the two relaxation rates R 1 R_1 and R 2 R_2.

So, the saturation parameter \(S = \frac{B_{12}\rho_\nu}{R^}\) *can be interpreted physically as the ratio of the light-induced transition rate, which is proportional to B 12 ρ ν* $B_{12}\rho_\nu$, to this effective relaxation rate, \(R^\). It's a direct measure of the competition between the laser pumping and the system's relaxation.

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Let's explore the physical meaning of the saturation parameter S S. Understanding its different limits is key to developing an intuition for saturation phenomena.

First, if S = 0 $S = 0$, this corresponds to the linear absorption limit. This happens if the laser intensity is zero. In this case, our formula Δ N = Δ N 0 1 + S $\Delta N = \frac{\Delta N^0}{1+S}$ gives Δ N = Δ N 0 $\Delta N = \Delta N^0$. The population difference is unchanged from its thermal equilibrium value.

Second, the case S = 1 $S = 1$. This is a crucial benchmark. When S = 1 $S = 1$, our formula gives Δ N = Δ N 0 1 + 1 = Δ N 0 2 $\Delta N = \frac{\Delta N^0}{1+1} = \frac{\Delta N^0}{2}$. This means the population difference has been reduced to exactly 50 percent of its unsaturated value. The intensity that is required to achieve S = 1 $S = 1$ is given a special name: the "saturation intensity," which we will denote I s I_s. So by definition, I s I_s is the intensity at which S = 1 $S = 1$.

Third, the case S ≫ 1 $S \gg 1$, meaning S S is much greater than one. This is the regime of "deep saturation." In this limit, the 1 1 in the denominator

of 1 + S $1+S$ is negligible, so Δ N ΔN approaches Δ N 0 S $\frac{\Delta N^0}{S}$, which becomes very small. The populations of the two levels nearly equalize. In some special cases with strong external pumping, it's even possible to achieve population inversion (N 2 > N 1 $N_2 > N_1$), where the medium can act as an amplifier, but for simple absorption, the populations just tend to equalize.

Finally, we need to express S S in a way that's easy to use in the lab. We don't measure energy density ρ ν ρ_ν; we measure intensity I I. So let's write an alternative expression for S S using measurable intensities.

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Here we see the conversion of the saturation parameter S S into a more practical form. We start with our definition: S = B 12 ρ ν R ∗ $S = \frac{B_{12}\rho_\nu}{R^*}$. We know the relationship between spectral energy density ρ ν ρ_ν and spectral intensity I ν I_ν is ρ ν = I ν c $\rho_\nu = \frac{I_\nu}{c}$. Substituting this in, we get:

S = B 12 I ν c R ∗

$$S = \frac{B_{12}\, I_\nu}{c\, R^*}$$

This is a perfectly valid form. However, what if our laser is very narrow-band? We often work with the total intensity I I, not the spectral intensity I ν I_ν. For a narrow laser with bandwidth δ ν L $\delta\nu_L$, we can approximate the total intensity as I ≈ I ν δ ν L $I \approx I_\nu\, \delta\nu_L$. This lets us write I ν ≈ I / δ ν L $I_\nu \approx I/\delta\nu_L$.

The slide shows a slightly different path to get to an expression with total intensity I I. The last equality shown is:

S = B 12 I c R 1 R 2

$$S = \frac{B_{12}\, I}{c\, R_1\, R_2}$$

Let's check the algebra here. The expression \(S = \frac{B_{12}\rho_{\nu}}{R^}\) *combined with the definitions* \(*R*^ = \frac{R_1 R_2}{R_1 + R_2}\) and I ≈ I v δ v L $I \approx I_\nu\, \delta\nu_{\mathrm{L}}$ ... ah, there seems to be a slight inconsistency or an unstated assumption in the slide's final step.

Let's stick to the most direct interpretation. We define the saturation intensity I s I_{s} such that S = I / I s $S = I/I_{\mathrm{s}}$. This is the most common and useful form. From the expression \(S = \frac{B_{12}\,I_{\nu}}{c\,R^}\)*, we can define a spectral saturation intensity* \(*I_{s,\nu} = \frac{c\,R*^}{B_{12}}\). Then S = I v / I s , v $S = I_\nu/I_{s,\nu}$. This is the most rigorous form. The conversion to total intensity I I depends on the relative widths of the laser and the absorption line, a point we will return to. For now, the key idea is that S S is directly proportional to the laser intensity.

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Let's formally define and explore the saturation intensity, I s I_{s}.

As stated in the first bullet point, it is defined by the condition S = 1 $S = 1$. It is the intensity required to reduce the population difference to half of its unsaturated value. It's the characteristic intensity scale for nonlinear effects in a given system.

From our previous discussion, we can write down a frequency-dependent, or spectral, form of the saturation intensity. Let's call it I s (v) $I_s(\nu)$. It is the spectral intensity required to reach S = 1 $S = 1$.

I s (v) = c R ∗ B 12

$$I_s(\nu) = \frac{c\,R^*}{B_{12}}$$

This shows us what I s I_s depends on: fundamental constants (c c), the atomic transition probability (B 12 B_{12}), and the relaxation environment of the system (hidden in R ∗ R^*).

Now, if we have a laser with a finite bandwidth δ v L $\delta\nu_L$, the total saturation intensity I s I_s is found by integrating the spectral saturation intensity over the laser's spectrum. Similar to our earlier approximation for total intensity, we can say:

I s = ∫ I s (v) d v ≈ I s (v L) δ v L

$$I_s = \int I_s(\nu)\,d\nu \;\approx\; I_s(\nu_L)\,\delta\nu_L$$

This is the total power per unit area we need from our laser to achieve S = 1 $S = 1$.

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This final point on saturation intensity is a crucial practical one for any experimentalist.

Knowledge of I s I_s is critical for two main reasons. First, for designing saturation experiments. If you want to perform saturation spectroscopy, you

need to know what I s I_s is for your transition of interest. This tells you how much laser power you need and how tightly you need to focus your beam to achieve an intensity I I that is comparable to or greater than I s I_s. If your laser system cannot deliver an intensity of at least I s I_s, you will not be able to saturate the transition and your experiment will fail.

Second, and equally important, is avoiding optical damage. Lasers can deliver very high intensities, especially when focused. For some materials, particularly solids or complex molecules, the saturation intensity might be close to or even above the optical damage threshold of the sample. You must ensure that the intensity you need for your experiment won't inadvertently destroy what you're trying to measure. So, calculating I s I_s beforehand is a critical safety and feasibility check.

Page 45: Saturation of Atomic Population Difference

This graph beautifully visualizes the concept of saturation. The title is "Saturation of Atomic Population Difference."

Let's look at the axes. The vertical axis is the Normalized Population Difference, which is the ratio Δ N Δ N 0 $\frac{\Delta N}{\Delta N^0}$. At zero intensity, this value is 1 1, meaning the population difference is its full, unsaturated value. The horizontal axis is the Incident Intensity, I I, plotted in units of the saturation intensity, I s I_s. So we have points for I s I_s, 2 I s $2\,I_s$, 3 I s $3\,I_s$, and so on.

The curve shows the function we derived: Δ N Δ N 0 = 1 1 + S $\frac{\Delta N}{\Delta N^0} = \frac{1}{1+S}$.

Since S = I I s $S = \frac{I}{I_s}$, this is equivalent to the equation shown on the plot:

Δ N Δ N 0 = 1 1 + I I s

$$\frac{\Delta N}{\Delta N^0} = \frac{1}{1 + \frac{I}{I_s}}$$

Let's trace the curve. At I = 0 $I = 0$, the ratio is 1 1. Now, let's go to the point on the x-axis labeled I s I_s. This is the saturation intensity. If we look up to the blue curve and then across to the y-axis, we see that the normalized population difference is 0.5 0.5. This is the very definition of I s I_s. It's the intensity needed to cut the population difference in half. The dashed red lines on the plot highlight this 50% reduction.

As we increase the intensity further, to 2 I s $2\,I_s$, 3 I s $3\,I_s$, and beyond, the curve continues to fall, asymptotically approaching zero. The population difference is being "squashed" by the strong laser field. This plot is the quantitative picture of "bleaching" the medium.

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Now let's incorporate our new understanding of saturation back into the absorption law itself.

Let's consider the specific case where our laser is narrower than the absorption line (δ v L < δ v a $\delta\nu_L < \delta\nu_a$). Our infinitesimal power balance equation was d P = − A I σ 12 Δ N d z $dP = -A\,I\,\sigma_{12}\,\Delta N\,dz$. We can now substitute our expression for the saturated population difference, Δ N = Δ

N 0 / (1 + S) $\Delta N = \Delta N^0/(1+S)$. This gives us the new, nonlinear absorption law:

d P = − A I σ 12 Δ N 0 1 + S d z .

$$dP = -A\, I\, \sigma_{12}\, \frac{\Delta N^0}{1+S}\, dz.$$

And since I = P A $I = P/A$, we could write:

d P P = − σ 12 Δ N 0 1 + S d z .

$$\frac{dP}{P} = -\frac{\sigma_{12}\, \Delta N^0}{1+S}\, dz.$$

Let's compare this with the linear case. The linear law is d P = − P σ 12 Δ N 0 d z $dP = -P\, \sigma_{12}\, \Delta N^0\, dz$, which gives d P P = − (σ 12 Δ N 0) d z $dP/P = -(\sigma_{12}\, \Delta N^0)\, dz$. The only difference is the factor of 1 / (1 + S) $1/(1+S)$ in the denominator. This factor is always less than or equal to 1, and it decreases as the intensity I I increases. This is the mathematical representation of saturation.

What is the qualitative effect? The third point is subtle but important. The absolute absorbed power, d P dP, still rises with intensity I I (at least initially), but the *relative* absorption, the fraction of power absorbed per unit length, which is d P / P dP/P, decreases. You get diminishing returns. Doubling a high intensity does not double the absorbed power.

This behavior is precisely what we observe experimentally as the fluorescence "bleaching" curve that we saw on slide 22. That curve is a direct plot of the consequences of this nonlinear absorption law.

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This slide addresses a very practical question: why is saturation spectroscopy synonymous with *laser* spectroscopy? Can't we achieve saturation with other light sources?

The answer lies in spectral intensity, I v I_ν. Let's look at the first point. Spectral lamps, like a sodium lamp or a mercury-vapor lamp, are what we call incoherent sources. They emit light over a broad range of angles and a relatively broad range of frequencies. Their spectral intensity I v I_ν is actually very small. If you plug the numbers into our formula for the saturation parameter S S, you will find that for any typical allowed atomic transition, S S is always much, much less than 1. The light from a lamp is simply not intense enough *at the specific resonant frequency* to significantly alter the populations. With conventional light sources, you are always in the linear absorption regime.

Now consider lasers. Lasers produce coherent light that is highly collimated and, for a single-mode laser, extremely monochromatic. This means they can achieve orders of magnitude higher spectral intensity I v I_ν. Furthermore, this light can be focused down to a tiny spot, increasing the intensity I I dramatically. With a typical continuous-wave laser, it is easy to achieve conditions where the saturation parameter S S is greater than or equal to 1.

Therefore, the inescapable conclusion is that saturation spectroscopy, and indeed almost all nonlinear spectroscopy, essentially requires lasers. The

laser is not just a convenient tool; it's the enabling technology that opened up this entire field of physics.

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We've established that lasers are what allow us to perform nonlinear spectroscopy, such as Doppler-free measurements and nonlinear mixing techniques. Now, we're going to pivot slightly and look at the interaction from a more microscopic, quantum-coherent perspective. This will introduce us to the Rabi frequency.

The title of this section is "Rabi Frequency, Ω R Ω_R – Microscopic Picture."

So far, we've used rate equations. Rate equations deal with populations, N 1 N_1 and N 2 N_2. They describe the interaction in terms of probabilities and rates, which is an incoherent picture. However, a more fundamental description, especially for short timescales, uses a semi-classical treatment where we consider the quantum atom interacting with a classical electromagnetic field.

In this picture, the oscillating electric field of the laser drives a coherent oscillation of the atom's electric dipole moment. This isn't just a random hopping between states; it's a deterministic, coherent evolution of the quantum amplitudes. The atom is driven back and forth between the ground and excited states. The angular frequency of this coherent population cycling is called the **Rabi frequency**, denoted capital Omega sub R, Ω R Ω_R.

The formula for the Rabi frequency is given as: Ω R = D i k E 0 ℏ $\Omega_R = \frac{D_{ik}E_0}{\hbar}$.

Ω R = D i k E 0 ℏ

$$\Omega_R = \frac{D_{ik}E_0}{\hbar}$$

Let's break this down. ℏ $\hbar$ is the reduced Planck constant. E 0 E_0 is the peak electric field amplitude of our laser, which we control. And D i k D_{ik} is the transition dipole matrix element.

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Let's elaborate on the terms in the Rabi frequency formula.

D i k D_{ik} is the transition dipole matrix element. Its formal definition is the matrix element of the electric dipole operator between the initial state | i ⟩ $|i\rangle$ and the final state | k ⟩ $|k\rangle$. It has units of charge times distance, and the slide gives its SI units as Coulomb-meters (C m) $(C\,m)$. This quantity, D i k D_{ik}, is a purely quantum mechanical property of the atom or molecule. It is calculated from the wavefunctions of the two states and it quantifies how strongly those two states are coupled by an electric field. Strong transitions have large dipole matrix elements. "Forbidden" transitions have dipole matrix elements that are zero or very close to zero.

The Rabi frequency, Ω R Ω_R, provides a crucial link. It relates a macroscopic, controllable experimental parameter—the laser's electric field E 0 E_0 (which is related to its intensity I I)—to the microscopic evolution of

the quantum amplitudes of the atom. It tells you, at a fundamental level, how fast the laser is "talking" to the atom.

Why is this important? It serves as a bridge between the rate-equation picture we've been using, with its saturation parameter S S, and the more advanced semi-classical picture described by the optical Bloch equations. The optical Bloch equations are a set of differential equations that describe the evolution of not just the populations, but also the coherent superposition between the states. The Rabi frequency is a central parameter in the Bloch equations.

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Now we arrive at a beautiful and insightful result that connects the two pictures we've been developing: the incoherent rate- equation picture (characterized by S S) and the coherent semi- classical picture (characterized by Ω R Ω_R). We can express the saturation parameter S S directly in terms of the Rabi frequency Ω R Ω_R.

Let's consider a system where the broadening is purely homogeneous. The homogeneous linewidth, γ γ, is the sum of the total decay rates of the two levels, so γ = R 1 + R 2 $\gamma = R_1 + R_2$. In this case, after some algebra which involves relating the Einstein B B coefficient to the dipole matrix element D i k D_{ik}, we find the following elegant relationship:

Capital S S equals Ω R 2 Ω_R^2, divided by the product R γ $R\gamma$. Which simplifies to Ω R 2 Ω_R^2, divided by R 1 R 2 $R_1 R_2$.

S = Ω R 2 R γ = Ω R 2 R 1 R 2 .

$$S = \frac{\Omega_R^2}{R\,\gamma} = \frac{\Omega_R^2}{R_1\,R_2}.$$

Let's focus on that final form: S = Ω R 2 R 1 R 2 $S = \frac{\Omega_R^2}{R_1 R_2}$.

This gives us a profound physical interpretation of saturation. Remember that saturation occurs when S S is on the order of 1. So, saturation is reached when Ω R 2 ≈ R 1 R 2 $\Omega_R^2 \approx R_1 R_2$, or Ω R ≈ R 1 R 2 $\Omega_R \approx \sqrt{R_1 R_2}$.

In words: saturation is achieved when the coherent driving rate (the Rabi frequency, Ω R Ω_R) becomes equal to the geometric mean of the relaxation rates of the two levels (R 1 R_1 and R 2 R_2). It's a competition! Ω R Ω_R is trying to coherently drive population back and forth, while R 1 R_1 and R 2 R_2 are the incoherent relaxation processes trying to destroy that coherence and restore thermal equilibrium. When the coherent driving is fast enough to overcome the relaxation, the system saturates.

The final bullet point rephrases this. The laser intensity I I that fulfills the condition Ω R 2 = R 1 R 2 $\Omega_R^2 = R_1 R_2$ corresponds precisely to the saturation intensity, I = I s $I = I_s$.

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Let's revisit and summarize the important distinction between closed and open two-level systems, as this has direct consequences for the saturation behavior.

First, a closed system. This is an idealized model, often a good approximation for a single, isolated atom. The key feature is that the total

population in our two levels of interest, capital N = N 1 + N 2 $N = N_1 + N_2$, is conserved. It's a constant. There are no external channels for population to leak out to or be pumped in from.

Second, an open system. This is the more realistic model for most experiments, like atoms in a vapor cell or molecules in a beam. Here, there are additional decay pathways (outflow) and pumping mechanisms (inflow), which we modeled with the C i C_i terms. Population is exchanged with the environment (the "reservoir levels").

This difference leads to a different mathematical form for the mean relaxation probability, or the effective relaxation rate, that governs saturation.

For a closed system, the relevant rate turns out to be the arithmetic mean, R = R 1 + R 2 2 $R = \frac{R_1+R_2}{2}$.

For the open system, as we derived, the effective rate is the harmonic mean, R ∗ = R 1 R 2 R 1 + R 2 $R^* = \frac{R_1 R_2}{R_1+R_2}$.

These might look similar, but they can lead to very different saturation intensities, especially if one relaxation rate is much larger than the other.

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What is the practical consequence of this difference between open and closed systems?

The consequence is that a stronger laser intensity is often needed to saturate an open system, particularly when external loss channels dominate.

Let's think about why. In an open system, you might have rapid relaxation or replenishment processes. For example, in a molecular beam, fresh, unsaturated molecules are constantly flying into the laser beam. To saturate the transition, your laser has to be intense enough to pump the molecules that are already there *and* the new ones that are continuously arriving. The inflow of fresh ground-state molecules is an additional channel that the laser has to "fight against" to deplete the ground state population. This means the denominator in the saturation parameter S S is effectively larger, and thus you need a larger numerator—a higher intensity I I—to achieve S = 1 $S = 1$.

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These two diagrams provide a clear side-by-side comparison of the closed and open two-level systems.

On the left, we have the "Closed Two-Level System." We see the two levels, | 1 ⟩ $|1\rangle$ and | 2 ⟩ $|2\rangle$. The laser drives the transition with a Rabi frequency Ω R Ω_R. The only relaxation path shown is spontaneous emission from | 2 ⟩ $|2\rangle$ back down to | 1 ⟩ $|1\rangle$, with a rate R 2 = A 21 $R_2 = A_{21}$. In this system, the crucial concept, written at the bottom, is that the total population N = N 1 + N 2 $N = N_1 + N_2$ is constant. Every atom that leaves level 1 must arrive in level 2, and vice versa. The population is just shuffled between these two levels.

On the right, we have the "Open Two-Level System." This looks more like a real experiment. We still have the laser driving the | 1 ⟩ $|1\rangle$ to | 2 ⟩ $|2\rangle$ transition with Rabi frequency Ω R Ω_R. We still have spontaneous emission A 21 A_{21}. But now we have additional channels. There's a pump term, Λ Λ, feeding population into the ground state | 1 ⟩ $|1\rangle$. This could be molecules entering the beam. There's also an additional loss channel from the upper state, γ loss γ_{loss}, which takes population out of the system entirely (e.g., decay to a third, dark state). And there is a loss rate R 1 R_1 from the ground state, for example atoms leaving the beam. As noted at the bottom, population is exchanged with the environment. The total decay rate from level 2 is now R 2 = A 21 + γ loss $R_2 = A_{21} + \gamma_{\text{loss}}$. The total population N 1 + N 2 $N_1 + N_2$ is no longer constant.

This visual comparison makes the distinction very clear.

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Let's analyze the limits of saturation in a closed system. What is the maximum possible transparency, or "bleaching," we can achieve? To find this, we look at the minimum possible population that can remain in the lower level, N 1 N_1, under very high laser intensity.

The slide presents the analytic solution for N 1 N_1 in a closed system under laser drive. The equation is:

N 1 = B 12 I ν c + R 2 2 B 12 I ν c + R 1 + R 2 2 N .

$$N_1 = \frac{\frac{B_{12} I_\nu}{c} + \frac{R_2}{2}}{\frac{B_{12} I_\nu}{c} + \frac{R_1 + R_2}{2}} N.$$

This expression comes from solving the steady-state rate equations with the constraint N 1 + N 2 = N $N_1 + N_2 = N$.

Now, let's consider the limiting case of infinite intensity. We take the limit as the spectral intensity I v I_ν goes to infinity. In the fraction, the terms with I v I_ν will dominate. The R / 2 $R/2$ terms become negligible. So the expression becomes

B 12 I v c B 12 I v c = 1.

$$\frac{\frac{B_{12} I_\nu}{c}}{\frac{B_{12} I_\nu}{c}} = 1.$$

However, we have to be careful with the algebra.

A more direct way to see this is that at infinite intensity, the rates of stimulated absorption and stimulated emission become infinitely fast compared to relaxation, forcing the populations to equalize, taking into account degeneracies. For non-degenerate levels, this means N 1 N_1 approaches N 2 N_2. Since N 1 + N 2 = N $N_1 + N_2 = N$, this implies N 1 N_1 approaches N / 2 $N/2$. The limit shown on the slide is correct: The limit of N 1 N_1 as I v I_ν approaches infinity is N / 2 $N/2$.

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This leads us to a very important conclusion about closed systems.

The result lim N 1 = N 2 $\lim N_1 = \frac{N}{2}$ means that the lower-level population cannot be depleted below 50 percent of the total population, no matter how strong your laser is.

Think about what this means for absorption. The population difference Δ N = N 2 − N 1 $\Delta N = N_2 - N_1$ approaches zero. The absorption coefficient α α approaches zero. However, you can never achieve population inversion, and you can't empty the ground state.

The key takeaway is that in a closed two-level atom, complete bleaching is impossible. The best you can do is make the populations equal, at which point the rates of absorption and stimulated emission exactly balance, and the medium becomes transparent. But you cannot get rid of all the atoms in the ground state, because the very same laser that removes them via absorption also puts them back via stimulated emission. The only way to truly empty the ground state is if there are external channels involved.

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Now let's contrast this with the situation in an open system. What is the minimum ground state population here?

The slide gives the solution for N 1 N_1 in the limit of very high saturation, S → ∞ $S \to \infty$, for the general open system rates.

The result is:

N 1 (S → ∞) = C 1 + C 2 R 1 + R 2 N .

$$N_1(S \to \infty) = \frac{C_1 + C_2}{R_1 + R_2} N.$$

This result is much more interesting than the closed system case. The final ground state population depends on the ratio of the total inflow rates (C 1 + C 2 $C_1 + C_2$) to the total outflow rates (R 1 + R 2 $R_1 + R_2$).

Now consider a very common experimental situation, like a molecular beam crossing a laser beam, where collisions are negligible. In this case, the main inflow C 1 C_1 is fresh molecules entering the beam into the ground state. There is no pumping into the upper state, so C 2 = 0 $C_2 = 0$. The main outflow R 1 R_1 is molecules leaving the beam. The outflow R 2 R_2 from the upper state includes spontaneous decay A 21 A_{21} and also decay to other "dark" vibrational levels that don't couple back into our system. If the inflow rates are much smaller than the relaxation rates (C 1 , C 2 ≪ R 1 , R 2 $C_1, C_2 \ll R_1, R_2$), which can be engineered, then the limiting population N 1 N_1 can approach zero!

This is the punchline. Hence, saturation can be much deeper in an open system. You can achieve almost complete bleaching, making the ground state population nearly zero.

This is essential for many advanced techniques, particularly for the background-free detection of very weak transitions. By pumping all the population out of the ground state, you create a very high-contrast "on/off" signal.

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Let's make this concrete with a detailed example of a molecular beam experiment. We will define the rate constants in terms of physical experimental parameters.

First, let's list the typical parameters.

The transit time, t τ t_τ, is the average time a molecule spends passing through the laser beam. If the beam has a diameter d d and the molecules have a velocity v v, then t τ = d v $t_\tau = \frac{d}{v}$.

The upper state, level 2, can decay via spontaneous emission with a total rate A 2 A_2. However, only a fraction of this decay may go back to our ground state, level 1. We define the branching ratio A 21 A_{21} as the rate of decay specifically from 2 to 1.

The inflow of fresh molecules is a diffusion or transit process. We can define a diffusion inflow rate D 1 D_1, which has units of number per volume per time. This rate is approximately equal to the total available number density N 0 N_0 divided by the transit time t τ t_τ. So, D 1 ≈ N 0 t τ $D_1 \approx \frac{N_0}{t_\tau}$.

Now we can replace the generic variables in our rate equations (R 1 R_1, R 2 R_2, C 1 C_1, C 2 C_2) with these specific physical processes.

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Here is how we map the experimental parameters from the molecular beam example onto our rate equation constants.

R 1 R_1: This is the total decay rate from the ground state. In a collision-free beam, the main way a ground state molecule leaves the interaction zone is by simply flying out of the laser beam. So, the rate R 1 R_1 is the inverse of the transit time.

R 1 = 1 t τ

$$R_1 = \frac{1}{t_\tau}$$

R 2 R_2: This is the total decay rate from the upper state. A molecule in the upper state can also fly out of the beam, so there is a transit-time contribution 1 / t τ $1/t_\tau$. Additionally, it can decay spontaneously with a total rate A 2 A_2. So, R 2 = A 2 + 1 / t τ $R_2 = A_2 + 1/t_\tau$.

R 2 = A 2 + 1 t τ

$$R_2 = A_2 + \frac{1}{t_\tau}$$

C 1 C_1: This is the inflow rate to the ground state. It has two contributions. First, there's the diffusion of new molecules into the beam, which we called D 1 D_1. Second, population from the upper state N 2 N_2 can decay back down to the ground state via spontaneous emission with rate A 21 A_{21}. So, C 1 = D 1 + N 2 A 21 $C_1 = D_1 + N_2 A_{21}$. Note that because this term depends on N 2 N_2, it makes the rate equations slightly more coupled than our initial general form.

C 1 = D 1 + N 2 A 21

$$C_1 = D_1 + N_2 A_{21}$$

C 2 C_2: This is the external pumping rate to the upper level. In a typical molecular beam absorption experiment, there is no such process. We are not actively pumping molecules into the excited state from outside. So, we can set C 2 = 0 $C_2 = 0$.

C 2 = 0

$$C_2 = 0$$

With these substitutions, we can now solve for the steady-state populations for this specific, realistic scenario.

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Alright, after substituting the specific rates for the molecular beam into the rate equations and solving for the steady-state population N 1 N_1 under laser drive, we get the rather formidable-looking expression shown on this slide.

N 1 = N D 1 (B 12 ρ + A 2 + 1 / t τ) B 12 ρ (A 2 − A 21 + 2 / t τ) + 1 / t τ 2 .

$$N_1 = N \frac{D_1(B_{12}\rho + A_2 + 1/t_\tau)}{B_{12}\rho(A_2 - A_{21} + 2/t_\tau) + 1/t_\tau^2}.$$

I don't expect you to memorize this. What's important is to understand its behavior in the limiting cases.

First limiting case: No laser. We set the energy density ρ ρ to zero. All the terms with B 12 ρ $B_{12}\rho$ vanish. The expression simplifies to

N 1 = D 1 (A 2 + 1 / t τ) 1 / t τ 2 .

$$N_1 = \frac{D_1(A_2 + 1/t_\tau)}{1/t_\tau^2}.$$

Assuming A 2 A_2 is not pathologically large, this can be shown to simplify to the result

N 1 0 = D 1 t τ .

$$N_1^0 = D_1\, t_\tau\,.$$

This makes perfect physical sense. With no laser, the steady-state ground population is simply the rate at which molecules enter (D 1 D_1) times the time they spend in the beam (t τ t_τ). This is our unsaturated reference population.

Second limiting case: Strong laser. This is the limit as the saturation parameter S S goes to infinity, which corresponds to ρ ρ going to infinity.

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Continuing with the strong laser limit for our molecular beam example.

As the energy density ρ ρ becomes very large, the terms multiplied by B 12 ρ $B_{12}\rho$ in our large expression for N 1 N_1 will dominate both the numerator and the denominator. So, N 1 N_1 will approach the ratio of the coefficients of the B 12 ρ $B_{12}\rho$ terms. This gives the approximation:

N 1 ≈ D 1 A 2 − A 21 + 2 t τ .

$$N_1 \approx \frac{D_1}{A_2 - A_{21} + \frac{2}{t_\tau}}.$$

The crucial thing to notice here is the comparison with the unsaturated population, N 1 0 = D 1 t τ $N_1^0 = D_1\, t_\tau$. The saturated population N 1 N_1 can be much, much smaller than N 1 0 N_1^0. For typical values, the denominator A 2 − A 21 + 2 t τ $A_2 - A_{21} + \frac{2}{t_\tau}$ can be a very large number, especially if the transit time is short. This means we can achieve a very strong depletion of the ground state. This confirms our earlier general conclusion: open systems can be bleached very deeply.

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Let's plug in some realistic numbers to get a feel for the magnitude of this effect. This numerical example is based on one from the Demtröder textbook.

Here are the parameters for our hypothetical molecular beam experiment: - The laser beam diameter is d = 1 $d = 1$ millimeter. - The velocity of the molecules is v = 5 × 10 4 $v = 5 \times 10^4$ centimeters per second, which is 500 meters per second, a typical thermal velocity. - This gives a transit time t τ = d / v = (1 m m) / (500 m / s) = 2 × 10 − 6 $t_\tau = d/v = (1\ \mathrm{mm})/(500\ \mathrm{m/s}) = 2 \times 10^{-6}$ seconds, or 2 microseconds.

The diffusion inflow rate is given as D 1 = 10 14 $D_1 = 10^{14}$ molecules per cubic centimeter per second.

From this, we can calculate the unsaturated ground state population density:

N 1 0 = D 1 t τ = (10 14 c m − 3 s − 1) × (2 × 10 − 6 s) = 2 × 10 8

$$N_1^0 = D_1\, t_\tau = (10^{14}\ \mathrm{cm^{-3}\,s^{-1}}) \times (2 \times 10^{-6}\ \mathrm{s}) = 2 \times 10^8$$

molecules per cubic centimeter.

Finally, we have the radiative rates for the transition. The total decay rate from the upper state is A 2 = 10 8 s − 1 $A_2 = 10^8\, s^{-1}$, corresponding to a 10 nanosecond lifetime. The specific decay rate back to our ground state is A 21 = 10 7 s − 1 $A_{21} = 10^7\, s^{-1}$. This means only 10% of the molecules that decay from the upper state return to the ground state; the other 90% decay to other "dark" reservoir levels. This is a classic open system.

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Now let's use the numbers from the previous slide to calculate the ground-state population in the limit of deep saturation.

We use our formula for the strong laser case:

N 1 ≈ D 1 A 2 − A 21 + 2 t τ .

$$N_1 \approx \frac{D_1}{A_2 - A_{21} + \frac{2}{t_\tau}}.$$

Plugging in the numbers:

D 1 = 10 14 c m − 3 s − 1 $D_1 = 10^{14}\,\mathrm{cm}^{-3}\,\mathrm{s}^{-1}$

A 2 = 10 8 s − 1 $A_2 = 10^{8}\,\mathrm{s}^{-1}$

A 21 = 10 7 s − 1 $A_{21} = 10^{7}\,\mathrm{s}^{-1}$

t τ = 2 × 10 − 6 s $t_\tau = 2 \times 10^{-6}\,\mathrm{s}$, so 2 t τ = 10 6 s − 1 . $\frac{2}{t_\tau} = 10^{6}\,\mathrm{s}^{-1}$.

The denominator is (10 8 − 10 7 + 10 6) s − 1 $(10^{8} - 10^{7} + 10^{6})\,\mathrm{s}^{-1}$, which is roughly 0.91 × 10 8 s − 1 $0.91 \times 10^{8}\,\mathrm{s}^{-1}$.

So, N 1 ≈ 10 14 0.91 × 10 8 ≈ 1.1 × 10 6 $N_1 \approx \frac{10^{14}}{0.91 \times 10^{8}} \approx 1.1 \times 10^{6}$ molecules per cubic centimeter.

The slide approximates this as N 1 ≈ 10 6 c m − 3 $N_1 \approx 10^{6}\,\mathrm{cm}^{-3}$.

Let's compare this to the unsaturated value, N 1 0 = 2 × 10 8 c m − 3 $N_1^0 = 2 \times 10^{8}\,\mathrm{cm}^{-3}$.

The ratio N 1 / N 1 0 N_1/N_1^0 is 10 6 / (2 × 10 8) = 0.005 $10^6/(2\times10^8) = 0.005$, or 0.5 percent!

This is a stunning result. In deep saturation, we have depleted the ground state population down to just half a percent of its initial value. This demonstrates the dramatic bleaching that is achievable in a collision-free, open-system environment like a molecular beam. This is what enables extremely high-contrast, low-background nonlinear spectroscopy.

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Now we will shift gears and calculate the saturation intensity I s I_s for a few different, practical cases.

Case (a) is a broadband continuous-wave, or CW, laser. "Broadband" here means that the laser's bandwidth, δ v L $\delta\nu_L$, is much, much greater than the absorption linewidth of an individual molecule, δ v a $\delta\nu_a$. δ v L ≫ δ v a $\delta\nu_L \gg \delta\nu_a$.

This is a common situation when doing spectroscopy on a Doppler-broadened sample in a gas cell with a multi-mode laser. The absorption linewidth for any single molecule (the homogeneous width) is small, but the laser talks to all the different velocity classes at once because its own bandwidth covers the entire Doppler profile.

The first point notes that the overlap fraction δ v a / δ v L $\delta\nu_a/\delta\nu_L$ is very small for any individual molecule, but the laser addresses all velocity classes simultaneously.

To find the total saturation intensity, we start from the condition S = 1 $S = 1$. Using our general expressions, we find that the total saturation intensity I s I_s is approximately:

I s ≈ c R ∗ B 12 δ v L

$$I_s \approx \frac{c\,R^*}{B_{12}}\,\delta\nu_L$$

The units are W m − 2 $\mathrm{W\,m^{-2}}$.

The key thing to see here is that I s I_s is directly proportional to the laser bandwidth δ v L $\delta\nu_L$. This makes sense: if your laser power is spread out over a large frequency range, you need more total power to achieve the required intensity *at the resonant frequency* to saturate the transition.

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Let's consider two important implications of our result for the broadband laser case.

First, the expression we derived for I s I_s is independent of the homogeneous or inhomogeneous nature of the underlying transition. Why? Because the laser bandwidth δ v L $\delta\nu_L$ is assumed to be so large that it covers the entire absorption profile, whether it's a single homogeneous line or a broad inhomogeneous collection of lines like a Doppler profile. The laser simply interacts with the entire ensemble at once.

Second, and this is a crucial point for experimentalists, this case highlights the importance of **spectral brightness**, not just total power. Spectral brightness is power per unit bandwidth. Our formula

I s ≈ c R ∗ B 12 ⋅ δ v L $I_s \approx \frac{c\,R^*}{B_{12}} \cdot \delta\nu_L$

shows that to achieve saturation (I ≈ I s $I \approx I_s$), what matters is the power you can deliver within the relevant atomic linewidth. A 1 Watt laser with a 100 GHz bandwidth may be less effective at saturating a transition than a 1 milliwatt laser with a 1 MHz bandwidth, because the latter has a much higher spectral brightness. It concentrates all of its power exactly where it's needed.

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Let's plug in some numbers for this broadband case, following Example 2.3 from the textbook.

We'll assume a laser bandwidth of δ v L = 3 × 10 9 s − 1 $\delta\nu_L = 3 \times 10^9\,s^{-1}$, which is 3 gigahertz. In terms of wavenumbers, which chemists and physicists often use, this is 0.1 c m − 1 $0.1\,cm^{-1}$. This is a typical bandwidth for a standard, non-stabilized dye laser or a multimode diode laser.

To calculate I s I_s, we need the Einstein B 12 B_{12} coefficient. We can relate B 12 B_{12} to the more commonly quoted spontaneous emission rate A 21 A_{21} using a standard formula from quantum mechanics. For a simple two-level system, this relation is:

B 12 = c 3 8 π h v 3 A 21 .

$$B_{12} = \frac{c^3}{8\pi h\nu^3} A_{21}.$$

Now, we substitute this expression for B 12 B_{12}, along with our molecular beam parameters for the relaxation rates R 1 R_1 and R 2 R_2, into our formula for I s I_s from the previous slide. After turning the crank on the arithmetic, we arrive at the result: The saturation intensity I s I_s is approximately 3 × 10 3 3×10^3 Watts per square meter.

Is this a lot? Let's see what it means in terms of total power. If we focus our laser beam down to a spot with an area A = 1 $A = 1$ square millimeter (1 m m 2 $1\,\mathrm{mm}^2$), the power P s P_s required to reach this saturation intensity is: P s = I s × A = (3 × 10 3 W / m 2) × (10 − 6 m 2) = 3 × 10 − 3 $P_s = I_s \times A = (3 \times 10^3\,\mathrm{W/m^2}) \times (10^{-6}\,\mathrm{m^2}) = 3 \times 10^{-3}$ Watts, or 3 milliwatts.

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The result of our calculation—that only 3 milliwatts of power is needed to saturate the transition in this broadband example—is very significant.

As the slide notes, this illustrates the feasibility of saturation spectroscopy with very modest, common laboratory lasers. Three milliwatts is well within the output power range of typical diode lasers, like the one in your laser pointer, or laboratory workhorses like dye lasers and Ti:sapphire lasers.

You don't need a giant, building-sized fusion laser to explore nonlinear optics. The high spectral brightness of even common, low-power lasers is more than sufficient to drive atomic and molecular transitions into the saturated regime, opening the door to a wide range of powerful spectroscopic techniques.

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Let's consider another important special case: matching the laser bandwidth to the homogeneous width of the transition. This represents the most efficient use of laser photons, as you're putting all the light exactly where the atoms can absorb it.

The condition is δ v L ≈ γ / 2 π $\delta\nu_{\mathrm{L}} \approx \gamma/2\pi$, where γ γ is the full-width at half-maximum of the homogeneous Lorentzian lineshape. For our molecular beam example, the homogeneous width γ γ is determined by the total decay rate from the upper state, A 2 A_2, and the transit time, which contributes to the broadening for both levels. The formula is γ = A 2 + 2 / t τ $\gamma = A_2 + 2/t_\tau$.

With this condition, we can derive a specific formula for the saturation intensity I s I_{s}. The algebra is a bit involved, but the result is:

I s = 4 h v 3 T A 21 c 2 (A 2 + 1 / t τ) .

$$I_{\mathrm{s}} = \frac{4\,h\,\nu^3}{T\,A_{21}\,c^2(A_2 + 1/t_\tau)}.$$

There seems to be a T T in the formula on the slide which is likely a typo and should not be there. Let's ignore it.

Plugging in our typical numbers for a visible transition, we arrive at a remarkable result: I s I_{s} is approximately 100 W / m 2 $100\ \mathrm{W/m^2}$. This is equivalent to 100 μ W / m m 2 $100\ \mu\mathrm{W/mm^2}$.

This is already 30 times lower than the saturation intensity we found for the broadband laser. We are using our photons much more efficiently.

Now, what if we focus the laser even more tightly? If we focus down to a tiny spot, 10 × 10 μ m 2 $10 \times 10\ \mu\text{m}^2$, which has an area of 10 − 10 m 2 $10^{-10}\ \text{m}^2$, the required power to reach saturation, P s P_s, is:

P s = I s × A = (100 W / m 2) × (10 − 10 m 2) = 10 − 8 W ,

$$P_s = I_s \times A = (100\ \text{W/m}^2) \times (10^{-10}\ \text{m}^2) = 10^{-8}\ \text{W},$$

which is 10 nanowatts.

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The result of that last calculation—that a saturation power of just 10 nanowatts is needed when the laser bandwidth is matched to the homogeneous width and tightly focused—is truly astounding.

This demonstrates the incredible propensity of narrow-band lasers to saturate even extremely weak transitions. Ten nanowatts is an exceptionally small amount of optical power. This means that if you have a stable, narrow-band laser, you can perform saturation spectroscopy on almost any allowed transition you can find. It underscores the power of concentrating your optical energy not just spatially (by focusing) but also spectrally (by using a narrow-band source). This is the key that unlocks the ability to study subtle effects and very weak transitions with high precision.

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Let's now analyze our final specific scenario, Case (b): a single- mode laser interacting with a simple atomic line.

First, let's lay out the assumptions. We assume the atomic line is homogeneously broadened. This means effects like Doppler broadening are absent, perhaps because we are using a cooled and trapped sample of atoms or a perpendicular atomic beam. We also assume that spontaneous emission is the dominant relaxation mechanism. This means we can neglect collisions and transit- time effects.

Under these conditions, the relaxation rates simplify greatly. The ground state is stable, so R 1 = 0 $R_1 = 0$. The upper state decays only via spontaneous emission back to the ground state, so R 2 = A 21 $R_2 = A_{21}$. Our effective relaxation rate R $*$ R^* was defined as R 1 R 2 R 1 + R 2 $\frac{R_1 R_2}{R_1 + R_2}$. Plugging in R 1 = 0 $R_1 = 0$ and R 2 = A 21 $R_2 = A_{21}$ seems to give zero, but we need to be more careful. This is a case of a closed two- level system. The relevant relaxation rate in the formula relating S S and Ω R Ω_R is R 1 R 2 $R_1 R_2$. If R 1 R_1 is zero... ah, we need to use the more general formula for a closed system.

Alternatively, the slide provides a result for \(R^*). *It states that for upper- state decay only via* A 21 A_{21}, the effective \(R^\) to be used is A 21 / 2 $A_{21}/2$. This comes from the proper treatment of a closed two- level system.

Now, we can consider the phenomenon of power broadening. When we drive a transition with a strong field, the transition itself appears broader. The saturation- broadened half- width of the transition at an intensity corresponding to S = 1 $S = 1$ is given by the formula...

The slide gives the saturation-broadened absorption linewidth δ v a $\delta\nu_a$ for this case. It is given by δ v a = 2 A 21 2 π $\delta\nu_a = \sqrt{\frac{2\,A_{21}}{2\pi}}$. This formula seems slightly unconventional. A more standard result for the power-broadened FWHM γ ′ γ' is γ ′ = γ 1 + S $\gamma' = \gamma\sqrt{1+S}$, where γ = A 21 2 π $\gamma = \frac{A_{21}}{2\pi}$ is the natural linewidth.

Let's focus on the second part of the slide, which is a classic and very useful result. We can derive the saturation intensity I s I_s directly from the S = 1 $S = 1$ condition. This requires relating the B 12 B_{12} coefficient to A 21 A_{21} and using the appropriate relaxation rates. When the algebra is done, we obtain the following classic formula for the saturation intensity of a two-level atom dominated by spontaneous emission:

I s = 2 2 h v A 21 λ 2

$$I_s = \frac{2\sqrt{2}\,h\,\nu\,A_{21}}{\lambda^2}$$

There seems to be an inconsistency in the formulas presented across slides. A more standard, and perhaps more memorable, formula often derived in this limit is

I s = π h c A 21 3 λ 3

$$I_s = \frac{\pi\,h\,c\,A_{21}}{3\,\lambda^3}$$

or

I s = 2 π 2 h c γ 3 λ 3 .

$$I_s = \frac{2\pi^2 h c \gamma}{3 \lambda^3}.$$

Let's proceed with the formula given on the slide, but be aware that different derivations can lead to slightly different numerical prefactors depending on the exact definitions of lineshape and width. The key dependencies are what matter.

I s I_s is proportional to h v $h\nu$ (the photon energy) and A 21 A_{21} (the decay rate), and inversely proportional to λ 2 λ^2 (the wavelength squared).

We also use the fundamental relation

λ = c v

$$\lambda = \frac{c}{\nu}$$

.

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Let's explore an alternative route to derive this saturation intensity, I s I_s, using the absorption cross-section. This is a great way to build confidence in our results; if we can arrive at the same answer from two different perspectives, we can be more certain that our theory is consistent.

First, let's look at the integrated line strength. We've already established the relationship between the integrated cross-section and the Einstein coefficients. Here it's written connecting B 12 B_{12} and A 21 A_{21}:

∫ σ 12 d v = h v c B 12 = c 2 8 π v 2 A 21 .

$$\int \sigma_{12}\, d\nu = \frac{h\nu}{c}\, B_{12} = \frac{c^2}{8\pi\nu^2}\, A_{21}.$$

This is a fundamental sum rule.

Now, for a purely lifetime-broadened transition, the lineshape is a Lorentzian. A Lorentzian has a peak value, σ (ν 0) $\sigma(\nu_0)$, and a full-width at half-maximum, γ γ. The area under a Lorentzian is related to the peak times the width. Specifically,

∫ σ (ν) d ν = π 2 σ (ν 0) γ .

$$\int \sigma(\nu)\, d\nu = \frac{\pi}{2}\, \sigma(\nu_0)\, \gamma.$$

The slide suggests a simpler approximation: peak value × width ≈ integral . peak value × width ≈ integral. So, σ (ν 0) γ ≈ c 2 8 π ν 2 A 21 . $\sigma(\nu_0)\,\gamma \approx \frac{c^2}{8\pi\nu^2}\, A_{21}$. We also know the natural linewidth is γ = A 21 2 π . $\gamma = \frac{A_{21}}{2\pi}$. We can solve this for the peak cross-section σ (ν 0) $\sigma(\nu_0)$.

Then, we can use an alternative definition for I s I_s, which is I s = h ν 2 σ (ν 0) τ s p $I_s = \frac{h\nu}{2\,\sigma(\nu_0)\,\tau_{sp}}$, where τ s p = 1 A 21 $\tau_{sp} = 1/A_{21}$. Plugging in our expression for σ (ν 0) $\sigma(\nu_0)$ should allow us to derive the same I s I_s.

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After performing the calculation using the cross-section method, we arrive at an expression for the saturation intensity I s I_s. The expression shown here is:

I s = 2 h ν A 21 λ 2

$$I_s = \frac{2h\nu A_{21}}{\lambda^2}$$

This result is derived without explicitly including the effects of saturation broadening in the definition, hence the note "(without saturation broadening)". It differs from the formula on Paage 70 by a factor of $2\sqrt{2}$. This highlights that numerical prefactors can vary depending on the approximations used (e.g., square lineshapes vs. Lorentzians, how broadening is handled). The key takeaway is that the physical dependencies—proportionality to $h\nu$ and A_{21}, and inverse proportionality to $\lambda 2$—remain robust.

The final point here is a crucial one in theoretical physics. Performing these kinds of consistency cross-checks, where we derive the same result from different starting points, provides confidence in our theoretical expressions. It shows that our framework of rate equations, Einstein coefficients, and cross-sections forms a coherent and self-consistent picture of reality.

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Let's end our theoretical development with one final numerical example, this time for a typical visible atomic line.

We will choose a wavelength $\lambda = 500$ nanometers, which is in the green part of the spectrum. We'll assume a strong, allowed transition with a spontaneous decay rate of $A_{21} = 10^8\, s^{-1}$, which corresponds to an excited state lifetime of 10 nanoseconds.

Now, let's evaluate the saturation intensity I_s using the formula from Paage 70:

I s ≈ 2 2 h c 2 A 21 λ 3 ,

$$I_{\mathrm{s}} \approx \frac{2\sqrt{2}\, h\, c^2\, A_{21}}{\lambda^3},$$

after substituting v = c / λ $\nu = c/\lambda$. The slide presents the result of this calculation as: I s ≈ 2.6 × 10 7 W / m 2 $I_{\mathrm{s}} \approx 2.6 \times 10^7\ \mathrm{W/m^2}$. This is 26 megawatts per square meter. This seems like a very high intensity.

As the slide notes, in a live lecture, we would work through the detailed arithmetic on the board to ensure all the constants and powers of 10 are correct. h ≈ 6.6 × 10 − 34 $h \approx 6.6 \times 10^{-34}$, c ≈ 3 × 10 8 $c \approx 3 \times 10^8$, A 21 = 10 8 $A_{21} = 10^8$, λ = 5 × 10 − 7 $\lambda = 5 \times 10^{-7}$.

I s ≈ 2.8 × 6.6 × 10 − 34 × 3 × 10 8 × 10 8 (5 × 10 − 7) 2 = 5.9 × 10 − 17 2.5 × 10 − 13 ≈ 2.4 × 10 − 4 W / m 2 .

$$I_{\mathrm{s}} \approx \frac{2.8 \times 6.6 \times 10^{-34} \times 3 \times 10^8 \times 10^8}{(5 \times 10^{-7})^2} = \frac{5.9 \times 10^{-17}}{2.5 \times 10^{-13}} \approx 2.4 \times 10^{-4}\ \mathrm{W/m^2}.$$

There is a major discrepancy between my calculation and the slide. Let's re-examine the formulas. Using I s = π h c A 21 3 λ 3 $I_{\mathrm{s}} = \frac{\pi\, h\, c\, A_{21}}{3\, \lambda^3}$:

I s = π × 6.6 × 10 − 34 × 3 × 10 8 × 10 8 3 × (5 × 10 − 7) 3 ≈ 1.6 × 10 2 W / m 2 .

$$I_{\mathrm{s}} = \frac{\pi \times 6.6 \times 10^{-34} \times 3 \times 10^8 \times 10^8}{3 \times (5 \times 10^{-7})^3} \approx 1.6 \times 10^2\ \mathrm{W/m^2}.$$

Let's trust the slide's calculation for now, as there may be a definition I'm missing, but always be critical of the numbers. Assuming I s ≈ 2.6 × 10 7 W / m 2 $I_{\mathrm{s}} \approx 2.6 \times 10^7\ \mathrm{W/m^2}$ is correct, let's see the power required.

If we focus this light to a 10 micrometer radius spot, the area is A = π r 2 ≈ 3.1 × 10 − 10 m 2 $A = \pi r^2 \approx 3.1 \times 10^{-10}\,\mathrm{m}^2$. The required saturation power P s P_s is then I s × A $I_s \times A$.

P s ≈ (2.6 × 10 7 W / m 2) × (3.1 × 10 − 10 m 2) ≈ 8.1 × 10 − 3 W .

$$P_s \approx (2.6 \times 10^7\,\mathrm{W/m^2}) \times (3.1 \times 10^{-10}\,\mathrm{m^2}) \approx 8.1 \times 10^{-3}\,\mathrm{W}.$$

The slide says 0.8 mW.

Ah, 2.6 × 10 3 W / m 2 $2.6 \times 10^3\,\mathrm{W/m^2}$ would give 0.8 μ W $0.8\,\mu\mathrm{W}$. 2.6 × 10 7 W / m 2 $2.6 \times 10^7\,\mathrm{W/m^2}$ gives 8 m W $8\,\mathrm{mW}$. It seems there are some typos in the slide's numbers. The key point, however, is that even for a high saturation intensity, the required *power* is typically in the milliwatt range or less due to the tight focusing, which is readily achievable.

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Let's consider how the saturation intensity changes with the strength of the transition. Our formulas show that I s I_s is directly proportional to A 21 A_{21}.

So, if we consider a weaker transition, for instance, one where A 21 = 10 7 s − 1 $A_{21} = 10^7\,s^{-1}$ (a 100 nanosecond lifetime) instead of 10 8 s − 1 $10^8\,s^{-1}$, the saturation intensity I s I_s will drop by the same factor of 10.

This might seem counter-intuitive at first. A weaker transition requires *less* intensity to saturate. Why? Because saturation is a competition between pumping and relaxation. For a weak transition, the relaxation rate A 21 A_{21} is slow. This means the atom, once excited, stays in the upper state for a long time. It doesn't take a very high pumping rate to keep up with this slow relaxation and deplete the ground state. For a strong transition, relaxation

is very fast, so you need a much more intense laser to pump the atoms faster than they can decay.

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Let's briefly discuss a couple of additional factors that are important in real experiments: collision broadening and the use of pulsed lasers.

First, collisions. In a gas cell, atoms are constantly colliding with each other or with a buffer gas. Each collision can interrupt the phase of the atomic wavefunction or induce a transition. This is an additional relaxation mechanism and it contributes to the homogeneous width of the transition. We can define a collisional broadening width, γ coll γ_{coll}. This adds to the other relaxation rates, so the total relaxation rate γ γ increases. Since the saturation intensity I s I_s is proportional to the relaxation rate (I s ∝ γ $I_s \propto \gamma$), increasing the pressure and thus the collision rate will increase the saturation intensity. This is why at high pressures, more laser power is needed to saturate a transition. Techniques like buffer-gas cooling can be used to mitigate this by slowing down the collisions.

Second, pulsed lasers. So far, we've mostly assumed continuous-wave (CW) lasers. But many experiments use pulsed lasers, which have very high peak power but are only on for a short duration, T L T_L (for example, nanoseconds or femtoseconds). If this pulse duration T L T_L is shorter than the population relaxation time (which is on the order of 1 / R $1/R$), then the system never reaches a steady state. Our steady-state rate equation analysis breaks down completely.

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When dealing with short laser pulses where the system does not reach steady state, we need a more sophisticated approach.

The effective saturation criterion must then be derived from the time-dependent solutions of the optical Bloch equations. The Bloch equations are a more complete semi-classical model that tracks the evolution of the population difference *and* the atomic coherence (the off-diagonal elements of the density matrix) as a function of time.

Solving these equations is beyond the scope of our current discussion, but the key conceptual difference is this: for CW saturation, we care about **intensity** (power per area, in Watts per square meter). For pulsed saturation, we care about **fluence** (energy per area, in Joules per square meter). You need to deliver a certain amount of *energy* in your pulse—often characterized by a "π-pulse" which has enough energy to completely invert the population—before the atom has time to relax.

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This graph provides a very clear comparison of saturation behavior for continuous-wave (CW) versus nanosecond pulsed excitation.

The axes are Normalized Signal (which could be the fraction of population in the excited state, N 2 / N N_2/N) versus the Average Laser Power.

The blue curve represents the CW laser. As we've discussed, it shows the classic saturation behavior. The system reaches a steady state where the

excitation rate is balanced by the relaxation rate. Saturation depends on the laser's *intensity* (in Watts per square meter).

The orange curve represents the pulsed laser. Notice that it rises much more steeply and saturates at a much lower *average* power. Why? Because the *peak* power of the pulse is enormous. Even though the laser is off most of the time, when it's on, it's incredibly bright. The text box for the pulsed laser explains that the pulse duration is shorter than the relaxation time, so the system is not in steady state. Significant population transfer can happen within a single pulse. Saturation now depends on the pulse *fluence* (in Joules per square meter).

The dashed lines show a comparison. To reach a signal level of 0.5, the CW laser requires an average power of about 400 arbitrary units. The pulsed laser achieves the same level of excitation with an average power of only about 50 units. This is because the pulsed laser can efficiently pump the population before relaxation has a chance to undo its work.

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Alright, let's summarize the key take-away messages from this entire lecture on linear and nonlinear absorption.

First, the saturation parameter, capital S S, is the central concept. It encapsulates the competition between light-induced excitation and the various relaxation processes in the system. The condition S = 1 $S = 1$, which occurs at the saturation intensity I s I_s, defines the operational boundary between the linear and nonlinear regimes. It's the point where the population difference is halved.

Second, the saturation intensity I s I_s is not a universal constant. It depends on many factors: the intrinsic transition probability of the atom (related to A 21 A_{21}), the laser bandwidth, the specific relaxation channels present in the environment (collisions, transit time), and the focusing geometry of the beam. You must calculate it for your specific experimental conditions.

Third, the distinction between open and closed systems is practically very important. Open systems, where population can leak out to a reservoir, can be "bleached" far more strongly than closed systems. This allows for the generation of very clear, high-contrast nonlinear signals, which is essential for many high-precision experiments.

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And the final, and perhaps most important, take-away message is a practical one.

The quantitative formulas we have derived today are not just abstract theoretical constructs. They are the essential tools that allow experimentalists to intelligently design their experiments. By using these formulas, you can calculate the required laser power, determine the optimal beam waist (focusing), and choose the right sample environment (e.g., a low-pressure cell or a molecular beam) to achieve the desired saturation conditions for optimal nonlinear-spectroscopic performance. This is theory put directly into practice.

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To help you solidify your understanding of these concepts, here are some suggested further exercises. I strongly encourage you to work through them.

1. Derive the saturation intensity I s I_s for a three-level Lambda-system. In a Lambda system, you have two ground states and one excited state. Imagine the upper level can decay preferentially to a third level, which is not the one you started from. How does this additional decay path, which makes the system very "open," affect the relaxation rates and the final expression for I s I_s?

2. Simulate the time-dependent saturation for a nanosecond pulse. This would involve numerically solving the optical Bloch equations (or at least the time-dependent rate equations) for a system with a given Rabi frequency, Ω R = 10 9 s − 1 $\Omega_R = 10^9\, s^{-1}$, and relaxation rates R 1 = R 2 = 10 6 s − 1 $R_1 = R_2 = 10^6\, s^{-1}$. You could plot the upper state population N 2 N_2 as a function of time during and after the pulse.

3. This is a practical challenge. Think about how you would perform Doppler-free saturation spectroscopy on iodine vapor, a classic experiment. Using the formulas we discussed from slides 30 to 34, estimate the laser power you would need. You'll have to look up the relevant parameters for the iodine transitions, like A 21 A_{21} and the Doppler width at room temperature.

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And a fourth exercise for those who are particularly ambitious:

4. Explore the impact of power broadening on frequency-stabilization schemes. A very common technique for locking a laser's frequency to an atomic transition is the Pound-Drever-Hall (PDH) method. This method relies on probing the sharp dispersive feature of the transition. However, as you increase the laser power to get a better signal-to-noise ratio, you also power-broaden the transition. How does this broadening affect the slope of the error signal in a PDH lock, and what are the trade-offs between signal strength and locking accuracy? This is a very real problem in experimental physics.

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Finally, I want to acknowledge the sources for this material and provide you with references for further reading.

The primary source for much of this lecture, and indeed for this entire course, is the quintessential textbook in the field: Wolfgang Demtröder's "Laser Spectroscopy." I am using the 5th edition, published by Springer. If you buy one book on this subject, this should be it. It's comprehensive, clear, and covers both the fundamental theory and the experimental details.

For supplementary reading, I highly recommend a few other classics.

Sargent, Scully, and Lamb's "Laser Physics" is a more advanced, deeply theoretical treatment, especially good if you want to dive into the quantum mechanics and the density matrix formalism.

Haken and Wolf's "Molecular Physics and Elements of Quantum Chemistry" provides an excellent bridge between the worlds of physics and chemistry and has very clear explanations of many fundamental concepts.

That concludes our lecture for today. Please review these concepts and have a look at the exercises. Next time, we will use this foundation in saturation to build our first Doppler-free spectroscopic technique. Thank you.