Chapter

3.0

Page 1:

Alright everyone, welcome to this segment of our Phys 608 Laser Spectroscopy course. I am Distinguished Professor Doctor M A Gondal, and today we embark on a crucial topic: Chapter 3, focusing on the Width and Profile of Spectral Lines.

Understanding the shapes and breadths of these lines is absolutely fundamental to interpreting spectroscopic data and, indeed, to the very essence of laser spectroscopy. We'll be delving into why spectral lines are not infinitely sharp, what determines their characteristics, and how we can extract rich physical information from them.

So, let's begin.

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Let's start with the basics of spectral lines, and address the fundamental question: why are they never infinitely narrow?

The first point to establish, as you well know, is that spectroscopy, at its heart, detects discrete transitions. These are transitions between quantized energy levels of atoms, molecules, or ions. When an electron jumps from a higher energy state to a lower one, it emits a photon. Conversely, it can absorb a photon to jump to a higher state. It's these energy packets, these photons, that we detect and analyze.

Now, in an idealized, almost naive picture, we might imagine that each specific transition corresponds to a perfectly defined energy difference. If the energy difference is precisely ΔE, then the emitted or absorbed photon should have a single, unique frequency, which we'll call ν_0 (ν_0), or equivalently, a single wavelength, λ_0 (λ_0). This follows directly from the Planck-Einstein relation, $E = h\nu$ ($E = h\nu$). So, if ΔE is perfectly sharp, ν_0 should also be perfectly sharp, leading to an infinitely narrow spectral line – a delta function in the frequency domain.

However, the third point brings us to the reality of the laboratory. When we actually perform an experiment and measure the intensity of light associated with a spectral transition, we find that the intensity is *not* concentrated at a single frequency. Instead, it is distributed over a small, but undeniably *finite*, frequency interval. We represent this distribution as $I(\nu)$ ($I(\nu)$), an intensity function that varies with frequency. This is the experimentally observed spectral line, and it always has some width. The core question of this chapter is: what gives rise to this width? Why isn't it a perfect spike?

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Continuing from our observation that spectral lines have a finite width, the immediate consequence is profound. Every "spectral line" we observe possesses a measurable width and, just as importantly, a characteristic shape, which we call its profile. This width and profile are not just artifacts; they are rich carriers of physical information. They tell us about the environment of the atoms or molecules, about their interactions, their motion, and even about the fundamental nature of quantum mechanics itself.

Understanding these widths and their corresponding profiles is absolutely essential in a wide array of scientific and technological fields. Let's look at a few examples to appreciate the scope:

First, precision metrology, particularly in the context of atomic clocks. The accuracy of an atomic clock is fundamentally linked to the narrowness and stability of the spectral line used as its reference. The narrower the line, the more precisely we can define a unit of time. So, understanding and minimizing line broadening is paramount here.

Second, these line shapes are critical for diagnostics of astrophysical and laboratory plasmas. When we look at the light from distant stars or from fusion experiments, the width and shape of spectral lines tell us about the temperature, density, and even the elemental composition of these incredibly hot and often turbulent environments. Different broadening mechanisms dominate under different plasma conditions, so a careful analysis of the line profile can unravel these parameters.

Third, in the realm of laser design and frequency stabilization. For a laser to operate efficiently and, crucially, at a very specific frequency, we need to understand the gain profile of the lasing medium, which is directly related to the spectral line shape of the transition involved. Stabilizing a laser's frequency to a very high degree often involves locking it to a narrow atomic or molecular reference line. Again, the characteristics of this reference line are key.

And fourth, understanding line shapes allows for fundamental tests of quantum electrodynamics, or QED. QED is our most precise theory of light-matter interactions. Some subtle QED effects, like the Lamb shift, actually manifest as small shifts or asymmetries in spectral lines. Measuring these with high precision requires a thorough understanding of all other contributions to the line shape and width, so we can isolate the QED effect.

So, you see, this isn't just an academic exercise. The width and profile of spectral lines have far-reaching implications.

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Let's now delve into the concept of Energy Levels and the Central, or Resonance, Frequency. This forms the basis for understanding where a spectral line is centered, before we even get to its width.

Consider a quantum system – this could be an atom, a molecule, or an ion. We're interested in two specific stationary states of this system. What do we mean by stationary states? These are states with well-defined energies, states that, in the absence of perturbations, do not change in time.

We'll label these states. There's an upper, or initial, state with energy E_i (E_i). The subscript 'i' can stand for 'initial'. The units of energy here are

Joules (J) in the S.I. system, though electronvolts (eV) or wavenumbers (cm^{-1}) are also commonly used in spectroscopy.

And there's a lower, or final, state with energy E_k (E_k). The subscript 'k' can represent the 'final' state in some conventions, or simply be an index distinct from 'i'. This state also has its energy in Joules.

Now, a transition between these two states involves an energy difference. This energy difference, ΔE (ΔE), must either be supplied to the system for absorption to occur (if the system goes from E_k to E_i), or it is released by the system during emission (if the system goes from E_i to E_k).

Mathematically, this energy difference is simply:

$$\Delta E = E_\text{i} - E_\text{k}$$

If E_i is greater than E_k, then ΔE is positive. This corresponds to emission if the system starts in state i and transitions to state k, releasing a photon of energy ΔE. If the system starts in state k and transitions to state i, it must absorb a photon of energy ΔE. The absolute magnitude of this energy difference is what's crucial for the photon involved.

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We've established the energy difference, ΔE, associated with a quantum transition. The next crucial step is to connect this energy to the frequency of the electromagnetic radiation – the light – that is either absorbed or emitted. This connection is given by the fundamental Planck-Einstein relation.

This relation states that the central frequency, ν_0, of the spectral line is given by:

$$\nu_0 = \frac{\Delta E}{h}$$

Let's break this down:

* ν_0 is the central, or resonance, frequency of the transition. This is the frequency where, ideally, the interaction between the light and the quantum system is strongest. Its units are Hertz (Hz), or cycles per second. * ΔE is the energy difference between the two quantum states involved, as we discussed, typically in Joules. * h is Planck's constant. Its value is given here as

$$h = 6.62607015 \times 10^{-34} \text{ J s}$$

It's important to note that since 2019, Planck's constant is a defined constant, used in the redefinition of the kilogram. It's a fundamental constant of nature, linking the energy of a photon to its frequency.

So, this ν_0 is what we often call the "line center." It's the characteristic frequency we associate with a specific atomic or molecular transition.

Now, in spectroscopy, and particularly in theoretical treatments involving quantum mechanics, it's often more convenient to work with angular frequency, ω, rather than the ordinary frequency ν. The reason for this will become clearer later, but it primarily helps to eliminate factors of 2π that frequently appear in equations.

The relationship between angular frequency ω_0 and ordinary frequency ν_0 is:

$$\omega_0 = 2\pi\nu_0$$

The units of angular frequency are radians per second (rad s^{-1}). Since radians are dimensionless, this is often just written as inverse seconds (s^{-1}).

So, if we want to express the Planck-Einstein relation using angular frequency, we would write $\Delta E = \hbar\omega_0$, where $\hbar$ is the reduced Planck constant, $\frac{h}{2\pi}$. This form is very common in quantum mechanics.

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Continuing our discussion on frequency notation, this slide underscores a practical point you'll encounter frequently in spectroscopy literature.

The bullet point states: "In spectroscopy literature, using ω is often more convenient for quantum-mechanical expressions involving phases $e^{-i\omega t}$."

Let's unpack why this is the case. Quantum mechanics describes particles, like electrons, using wavefunctions. The time evolution of these wavefunctions often involves phase factors. For a state with energy E, its time-dependent phase factor is $e^{-iEt/\hbar}$ ($e^{-iEt/\hbar}$). Using the relation $E = \hbar\omega$, this phase factor becomes simply $e^{-i\omega t}$ ($e^{-i\omega t}$). Notice how clean that looks! If we were to use ordinary frequency ν, the phase factor would be $e^{-i2\pi\nu t}$ ($e^{-i2\pi\nu t}$). That extra factor of 2π would appear in many, many equations, making them more cumbersome.

This convenience extends to Fourier transforms, which are fundamental in relating time-domain signals to frequency-domain spectra, and also in perturbation theory, where energy denominators often involve differences of frequencies. Using ω consistently simplifies the mathematical formalism in these areas.

So, while ν in Hertz might be more intuitive when thinking about experimental frequencies, ω in radians per second often makes the underlying quantum mechanical equations look more elegant and easier to manipulate. We'll see more examples of this as we progress. For now, just be aware that both notations are used, and it's important to be comfortable converting between them. The dashes at the bottom of the slide suggest this is a continuation or a pause before a new idea, which is indeed the case as we'll move to define the line profile next.

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Now that we've discussed the central frequency of a spectral line, let's formally define the concept of the Line Profile, which we denote as $I(\nu)$.

The first point states that the line profile, $I(\nu)$, represents the experimentally recorded intensity as a function of frequency, ν. When you set up a spectrometer and scan across a spectral feature, what you measure is how the intensity of light (either absorbed or emitted) changes as you tune your detection frequency. That measured curve of intensity versus frequency *is* the line profile. It's the "shape" of the spectral line that we talked about earlier. The notation $I(\nu)$ is explicitly shown enclosed in a box, emphasizing its definition.

The units of this intensity, $I(\nu)$, can vary quite a bit depending on the specific experimental setup and the type of detector used.

For example:

* If you are measuring spectral irradiance, the units might be Watts per square centimeter per Hertz $\(\mathrm{W\,cm^{-2}\,Hz^{-1}}$\). This tells you the power per unit area per unit frequency interval. * In photon counting experiments, which are common in many laser spectroscopy applications, the intensity might be recorded as counts per second $\(\mathrm{counts\,s^{-1}}$\), or counts per second per frequency interval. * Other units are also possible, such as Joules per cubic meter per Hertz $\(\mathrm{J\,m^{-3}\,Hz^{-1}}$\) if you're talking about spectral energy density.

The key is that $I(\nu)$ represents how the strength of the signal varies with frequency, regardless of the specific units chosen for that strength.

Crucially, the central maximum of this observed intensity distribution, $I(\nu)$, occurs at or very near the resonance frequency, $\nu = \nu_0$, which we defined earlier from the energy level difference $\Delta E = h\nu_0$.

This ν_0 is the peak of the line profile.

So, to summarize the last point: The complete functional dependence $I(\nu)$ in the vicinity of this central frequency ν_0 is called the line profile. It’s not just the peak; it’s the entire curve – how the intensity rises, peaks, and then falls off as you move away from the central frequency. This profile contains a wealth of information, which we are about to explore.

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Continuing our discussion on the line profile, $I(\nu)$, let's consider how we model these shapes and what they tell us.

The first bullet point mentions common analytical models that are used to describe these line profiles. We will study these in detail in later slides, but for now, it's good to be aware of their names:

* **Lorentzian:** This profile arises from several broadening mechanisms, most notably natural broadening (due to finite lifetimes of excited states) and collisional or pressure broadening. It has characteristic "wings" that fall off relatively slowly. * **Gaussian:** This profile is characteristic of Doppler broadening, which results from the random thermal motion of the atoms or molecules emitting or absorbing light. It falls off more rapidly in the wings compared to a Lorentzian. * **Voigt:** Often, in real systems, both Lorentzian and Gaussian broadening mechanisms are present simultaneously. The Voigt profile is a convolution of a Lorentzian and a Gaussian profile, and it's frequently needed to accurately model experimental line shapes, especially in gases at moderate pressures.

There are other, more complex models as well, but these three are the workhorses of line shape analysis.

The second bullet point is absolutely key: The profile, $I(\nu)$, encodes the physical broadening mechanisms at play. A spectral line is not just a peak; its specific shape – how wide it is, how quickly its wings decay, whether it's symmetric or asymmetric – provides deep insights into the physics of the system and its environment.

Let's list some of these broadening mechanisms that contribute to the overall line profile:

* **Natural lifetime:** This is a fundamental quantum mechanical effect. Excited states have finite lifetimes, which, via the energy-time uncertainty principle, leads to an inherent uncertainty in their energy, and thus a spread in the frequency of emitted photons. This typically results in a Lorentzian profile. * **Doppler shifts:** Atoms or molecules in a gas are in constant random motion. This motion causes Doppler shifts in the observed frequency of light – towards higher frequencies if moving towards the observer, and lower if moving away. The Maxwell-Boltzmann distribution of velocities leads to a Gaussian line shape. * **Collisions:** Interactions between the emitting/absorbing species and other particles (either of the same kind or different) can perturb the energy levels or interrupt the phase of the emitted/absorbed radiation. This is known as collisional or pressure broadening and often leads to a Lorentzian component. * **External fields:** The presence of external electric fields (Stark effect) or magnetic fields (Zeeman effect) can split or shift energy levels, leading to broadening or the appearance of multiple line components. * **Instrumental resolution:** Finally, the measuring instrument itself (spectrometer, interferometer) has a finite resolution. It cannot distinguish between infinitesimally close frequencies. This instrumental response function gets convolved with the true physical line shape, contributing to the observed width.

So, when we look at a spectral line, its profile is often a composite result of several of these mechanisms acting together. A significant part of laser spectroscopy involves carefully designing experiments to isolate these effects or using sophisticated line shape analysis to deconvolve them and extract the underlying physics.

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Alright, let's take a moment to visualize what we've been discussing. On this page, we have a graph that represents a typical spectral line profile.

Let's examine the axes first. The horizontal axis is labeled "Frequency (ν)" and its units are given as Hertz (Hz). This represents the frequency of the light we are observing or measuring. The vertical axis is labeled "Intensity (I)" and the units are described as "arbitrary units." This is common for schematic diagrams because, as we discussed, the specific units of intensity can vary. What's important here is the relative intensity at different frequencies.

Now, looking at the curve itself, it's a bell-shaped curve, which is characteristic of many spectral lines. • It starts at a low intensity at low frequencies (far left). • As the frequency increases, the intensity rises, reaching a peak at a specific frequency labeled ν_0 (nu sub zero). This ν_0 is our central or resonance frequency, the point of maximum intensity. The intensity at this peak is labeled $I(\nu_0)$ (I of nu sub zero) on the vertical axis. • As the frequency continues to increase beyond ν_0, the intensity falls off, eventually approaching zero at very high frequencies (far right).

The graph also highlights some important points for defining the width of this line, which we'll discuss formally in the next slide. You can see a horizontal dashed line drawn at an intensity level of $\frac{I(\nu_0)}{2}$ (I of nu sub zero divided by two), which is exactly half of the peak intensity. This dashed line intersects the line profile at two points. • The frequency at the intersection on the lower frequency side (left of ν_0) is labeled ν_1 (nu sub one). • The frequency at the intersection on the higher frequency side (right of ν_0) is labeled ν_2 (nu sub two).

These two frequencies, ν_1 and ν_2, are crucial because they define the points where the line's intensity has dropped to half its maximum value. The difference between ν_2 and ν_1 is what we will soon define as the Full Width at Half Maximum, or FWHM. This graph provides a clear visual representation of these key features of a spectral line profile. The shape depicted here looks somewhat like a Lorentzian or perhaps a Voigt profile, with fairly extended wings.

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Now that we have a visual understanding of a line profile from the previous graph, let's formally define one of the most common and practical measures of a spectral line's breadth: the Full Width at Half Maximum, often abbreviated as FWHM.

The first step, as highlighted on the previous graph and stated here, is to identify the two frequencies where the intensity of the spectral line, $I(\nu)$ (I(v)), drops to exactly one-half of its peak value. Let ν_0 (nu sub zero) be the frequency at which the intensity is maximum, $I(\nu_0)$. We are looking for two frequencies, ν_1 (nu sub one) and ν_2 (nu sub two), such that the intensity at these frequencies is equal to half the peak intensity. Mathematically, this is expressed as:

$$I(\nu_1) = I(\nu_2) = \frac{I(\nu_0)}{2}$$

Typically, ν_1 will be less than ν_0, and ν_2 will be greater than ν_0, assuming a symmetric line shape, though the definition holds even for asymmetric lines.

Once we have these two frequencies, ν_1 and ν_2, the Full Width at Half Maximum, which we'll denote by the symbol $\delta\nu$ (delta nu), is simply the difference between them. Since width must be a positive quantity, we take the absolute value:

$$\delta\nu = |\nu_2 - \nu_1|$$

This $\delta\nu$ (delta nu) is the FWHM. It represents the full span in frequency over which the line's intensity is greater than or equal to half its maximum intensity. It's a very convenient and widely used metric because it gives a single number that characterizes the "width" of the line. A smaller $\delta\nu$ implies a narrower, more sharply defined spectral line, which is often desirable in high-resolution spectroscopy. Conversely, a larger $\delta\nu$ indicates a broader line, which might be due to one or more of the broadening mechanisms we mentioned earlier.

The FWHM is a direct, measurable quantity from an experimental spectrum, as we saw on the graph.

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Let's continue with some important notes regarding the Full Width at Half Maximum, or FWHM.

The first point mentions an alternative symbol often used for FWHM, especially in quantum optics. The symbol Γ (capital Gamma) is frequently used to denote the FWHM, or sometimes the half-width at half-maximum (HWHM) depending on context, especially when discussing decay rates or natural linewidths. So, if you see Γ in the context of spectral lines, it's very likely related to the line's width. It's always good practice to check the definition being used in any specific text or paper.

The second point introduces another related quantity: the Half-Width at Half-Maximum, or HWHM. As the name suggests, the HWHM is simply half of the FWHM. So, HWHM equals $\frac{\delta\nu}{2}$. While the HWHM is a perfectly valid quantity, it is generally less commonly used in general optics and spectroscopy literature compared to the FWHM. The FWHM, being the *full* width, is often more directly comparable to, for example, the bandwidth of filters or the resolution of instruments.

The third point emphasizes the practical utility of the FWHM. It is the most practical single-number characterization of a line's breadth. Why is it so practical? Firstly, it can be directly read off a plotted spectrum. As we saw in the diagram on page 9, you find the peak, go down to half the height, and measure the width there. This makes it very intuitive and easy to determine experimentally. Secondly, if you have an analytical model for your line shape (like a Lorentzian or Gaussian), the FWHM can be precisely related to the parameters of that model. So, it can also be fitted mathematically from the data, providing a robust measure of the width.

For these reasons, FWHM is the go-to parameter for describing spectral linewidths in a vast number to contexts. The dashes here indicate we're pausing before moving to a new aspect, which will be converting FWHM between different units.

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Now, let's discuss how to convert the Full Width at Half Maximum (FWHM) between different, but related, physical quantities: specifically, between frequency, angular frequency, and wavelength.

Slide 5: Converting FWHM Between Frequency, Angular Frequency, and Wavelength

First, let's tackle the conversion between Frequency (ν, in Hertz) and Angular Frequency (ω, in radians per second). This is labeled as "1. Frequency ↔ Angular Frequency".

The fundamental definition linking these two quantities, as we've seen before, is:

$$\omega = 2\pi\nu$$

Here, ω (omega) is the angular frequency, and ν (nu) is the ordinary frequency. The factor of 2π (two pi) arises because there are 2π radians in one full cycle.

Now, if we are interested in small changes or widths, like the FWHM, we can consider how a small change in ν, let's call it $\delta\nu$ (delta nu), relates to a corresponding small change in ω, let's call it $\delta\omega$ (delta omega). Assuming 2π is a constant, we can simply say that for small differentials or for finite widths (like the FWHM), the relationship is:

$$\delta\omega = 2\pi\delta\nu$$

So, if you know the FWHM in Hertz (which is $\delta\nu$), you can find the FWHM in radians per second (which is $\delta\omega$) by simply multiplying by 2π.

Conversely, if you have $\delta\omega$, you divide by 2π to get $\delta\nu$. This conversion is straightforward due to the linear relationship between ω and ν. This is a very common conversion, especially when moving between experimental results (often quoted in Hertz or Megahertz or Gigahertz) and theoretical expressions (often derived in terms of ω).

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Next, let's address the conversion of FWHM between Frequency (ν) and Wavelength (λ). This is labeled as "2. Frequency ↔ Wavelength".

The starting point for this conversion is the dispersion relation for light in a vacuum. This fundamental equation relates the speed of light (c), the frequency (ν), and the wavelength (λ) of an electromagnetic wave: \\[c = \nu \lambda

(c = \nu \lambda)

Here, 'c' is the speed of light in vacuum. Its defined value is exactly c equals two hundred ninety-nine million, seven hundred ninety-two thousand, four hundred fifty-eight meters per second (c = 2.99792458 \times 10^{8}\, \text{m s}^{-1}). This value is exact because the meter is defined in terms of the speed of light.

Now, we want to relate a small change (or width) in frequency, \delta \nu (delta nu), to a corresponding small change (or width) in wavelength, \delta \lambda (delta lambda). To do this, we can differentiate the dispersion relation c = \nu \lambda . Since c is a constant, its differential is zero. We use the product rule for differentiating \nu \lambda : d(\nu \lambda) = \lambda\, d\nu + \nu\, d\lambda

(d(\nu \lambda) = \lambda\, d\nu + \nu\, d\lambda)

Setting the differential of c to zero, we get: 0 = \lambda\, d\nu + \nu\, d\lambda

(0 = \lambda\, d\nu + \nu\, d\lambda)

Or, using finite small changes \delta \nu and \delta \lambda instead of infinitesimals d\nu and d\lambda , we can write: 0 \approx \lambda\, \delta \nu + \nu\, \delta \lambda

(0 \approx \lambda\, \delta \nu + \nu\, \delta \lambda)

For small enough widths, this approximation becomes very good.

The slide asks us to solve for \delta \lambda (delta lambda). Rearranging the equation, we get: \nu\, \delta \lambda = -\lambda\, \delta \nu

(\nu\, \delta \lambda = -\lambda\, \delta \nu)

And from this, we can isolate \delta \lambda . We'll see the result on the next page. This process of differentiation is a standard way to relate small changes in variables that are connected by a formula.

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Continuing from the previous page, where we had the relation zero equals lambda delta nu plus nu delta lambda (0 = \lambda \delta \nu + \nu \delta \lambda), we can now solve for \delta \lambda (delta lambda), the change in wavelength corresponding to a change in frequency \delta \nu (delta nu).

Rearranging, we get:

\delta \lambda = -\frac{\lambda\, \delta \nu}{\nu}

Now, we can make this expression look a bit more common. We know from the dispersion relation that \lambda = \frac{c}{\nu} (λ = c/v), or equivalently, \nu = \frac{c}{\lambda} (v = c/λ). Let's substitute \nu = \frac{c}{\lambda} into the denominator:

\delta \lambda = -\frac{\lambda\, \delta \nu}{c/\lambda}

This simplifies to:

\delta \lambda = -\frac{\lambda^2\, \delta \nu}{c}

Alternatively, and as shown on the slide, we can substitute $\lambda = \frac{c}{\nu}$ into the numerator of the first expression: $\delta\lambda$ equals minus (c divided by nu) times δv all divided by nu.

$$\delta \lambda = -\frac{(c/\nu)\, \delta \nu}{\nu}$$

Which gives:

$$\delta \lambda = -\frac{c}{\nu^2}\, \delta \nu$$

This is the form presented on the slide. Both expressions are equivalent.

Let's discuss the negative sign. The negative sign indicates that an *increase* in frequency ($\delta \nu > 0$) corresponds to a *decrease* in wavelength ($\delta \lambda < 0$), and vice-versa. This is intuitive: higher frequency means shorter wavelength. However, when we talk about widths, like FWHM, we are interested in the magnitude of this spread. Widths are inherently positive quantities.

Therefore, when we calculate the magnitude of the wavelength FWHM, which we denote as the absolute value of $\delta \lambda$ ($|\delta\lambda|$), we take the absolute value of the expression:

$$|\delta \lambda| = \frac{c}{\nu^2} |\delta \nu|$$

Or, using the other form involving λ :

$$|\delta \lambda| = \frac{\lambda^2}{c} |\delta \nu|$$

Often, when ν is the central frequency ν_0 , and λ is the central wavelength λ_0 , we write:

$$|\delta \lambda| = \frac{\lambda_0^2}{c} |\delta \nu|$$

Or, the absolute value of $\delta \lambda$ equals c divided by nu sub zero squared, all times the absolute value of δv.

$$|\delta \lambda| = \frac{c}{\nu_0^2} |\delta \nu|$$

This formula is extremely useful for converting a frequency width (like a laser linewidth specified in MHz) into a wavelength width (in picometers or nanometers).

Finally, the slide mentions typical laboratory usage. Wavelength \lambda (lambda) is often expressed in nanometers (nm, 10^{-9} meters) or Angstroms (Å, 10^{-10} meters) for visible and UV light. Frequency \nu (nu) for optical transitions is very high, typically in the Terahertz range (THz, 10^{12} Hz). For example, visible light around 500 nanometers has a frequency of about 600 Terahertz. The corresponding wavelength width, \delta \lambda (delta lambda), for typical optical transitions, often lies in the picometer range (pm, 10^{-12} meters). For instance, a laser linewidth of a few Megahertz (MHz, 10^6 Hz) in the visible spectrum corresponds to a \delta \lambda of femtometers (fm, 10^{-15} meters) to picometers. The slide says picometers, which is a good general range to keep in mind for many common linewidths encountered in spectroscopy.

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Now we move to Slide 6, which introduces the concept of Unit-Independent Relative Halfwidths. This is a very powerful idea for comparing spectral features across different frequency or wavelength ranges.

The first point defines the relative (dimensionless) width for any variable x . If x is some quantity (like frequency \nu , angular frequency \omega , or wavelength \lambda), and \delta x (delta x) is its width (e.g., FWHM), then the relative width is defined as:

\left|\frac{\delta x}{x}\right|

This quantity is dimensionless because both \delta x and x have the same units, so they cancel out. For example, if frequency \nu is in Hertz and \delta \nu is in Hertz, then \frac{\delta \nu}{\nu} is unitless. This makes it a very convenient way to express "how wide" something is in proportion to its central value.

The second point is a key result. It states that starting with $x = \nu$ (our frequency) and using the conversions we've just discussed, we can prove a very elegant equality:

$$\left|\frac{\delta \nu}{\nu}\right| = \left|\frac{\delta \omega}{\omega}\right| = \left|\frac{\delta \lambda}{\lambda}\right|$$

Let's think about why this must be true. For frequency ν and angular frequency ω , we know $\omega = 2\pi\nu$. Therefore, $\delta \omega = 2\pi\delta \nu$. So,

$$\frac{\delta \omega}{\omega} = \frac{2\pi\delta \nu}{2\pi\nu} = \frac{\delta \nu}{\nu}$$

The 2π factors cancel perfectly. So, the first equality, $\left|\frac{\delta \nu}{\nu}\right| = \left|\frac{\delta \omega}{\omega}\right|$, is straightforward.

The third point on the slide begins a derivation example, specifically for $\nu \rightarrow \omega$, which we just mentally walked through. $\frac{\delta \omega}{\omega}$ equals $\frac{2\pi \times \delta \nu}{2\pi \times \nu}$, which simplifies to $\frac{\delta \nu}{\nu}$. So, the relative width in terms of angular frequency is indeed identical to the relative width in terms of ordinary frequency.

We'll look at the $\nu \rightarrow \lambda$ conversion on the next slide to complete the proof of the second equality. The beauty of this result is that if you calculate the relative width using any one of these representations (ν , ω , or λ), you immediately know it for the others.

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Let's continue with the derivation of the equality of relative widths, focusing now on the relationship between the relative width in frequency $\frac{\delta \nu}{\nu}$ and the relative width in wavelength $\frac{\delta \lambda}{\lambda}$.

The slide provides the derivation example for $\nu \to \lambda$. It reminds us to use the relation $\nu=\frac{c}{\lambda}$ (nu equals c divided by lambda), or equivalently, $\lambda=\frac{c}{\nu}$.

From our earlier work on page 14, we found the relation for the magnitudes of the widths:

$$|\delta \lambda| =\frac{c}{\nu^2}|\delta \nu| \quad \text{or equivalently} \quad |\delta \lambda| =\frac{\lambda^2}{c}|\delta \nu|$$

Let's use the first form: $|\delta \lambda| =\frac{c}{\nu^2}|\delta \nu|$.

Now, to find the relative wavelength width, $\frac{|\delta \lambda|}{\lambda}$, we divide by λ:

$$\frac{|\delta \lambda|}{\lambda} = \frac{\left(\frac{c}{\nu^2}|\delta \nu|\right)}{\lambda}$$

Substitute $\lambda=\frac{c}{\nu}$ into this expression:

$$\frac{|\delta \lambda|}{\lambda} = \frac{\left(\frac{c}{\nu^2}|\delta \nu|\right)}{\frac{c}{\nu}}$$

Now, let's simplify this. The 'c' in the numerator cancels with the 'c' in the denominator. One factor of ν in the denominator (from $\frac{c}{\nu}$) cancels with one factor of ν in ν^2 in the numerator's denominator.

So, we are left with:

$$\frac{|\delta \lambda|}{\lambda} = \frac{\left(\frac{1}{\nu}|\delta \nu|\right)}{1}$$

Which is simply:

$$\frac{|\delta \lambda|}{\lambda} = \frac{|\delta \nu|}{\nu}$$

The slide shows this derivation more compactly. It starts from

$$\frac{\delta \nu}{\nu}=-\frac{\delta \lambda}{\lambda},$$

which comes from differentiating $\ln (\nu)=\ln (c)-\ln (\lambda)$. If $\nu\lambda=c$, then

$$d(\nu\lambda)=0,$$

so

$$\delta \nu\cdot\lambda+\nu\cdot\delta \lambda=0.$$

Dividing by $\nu\lambda$ gives

$$\frac{\delta \nu}{\nu}+\frac{\delta \lambda}{\lambda}=0,$$

or

$$\frac{\delta \nu}{\nu}=-\frac{\delta \lambda}{\lambda}.$$

When we take the magnitudes, the negative sign disappears: The absolute value of $\frac{\delta \nu}{\nu}$ equals the absolute value of $\frac{\delta \lambda}{\lambda}$.

$$\left|\frac{\delta \nu}{\nu}\right|=\left|\frac{\delta \lambda}{\lambda}\right|$$

This confirms the second part of the equality we stated on the previous page.

So, we have now established that:

$$\left|\frac{\delta \nu}{\nu}\right|=\left|\frac{\delta \omega}{\omega}\right|=\left|\frac{\delta \lambda}{\lambda}\right|$$

The final bullet point highlights the immense practical importance of this result. Once the relative width is known in *any* one representation (frequency, angular frequency, or wavelength), it is immediately known in *all* others.

This is extremely convenient for comparing spectroscopy results obtained across vastly different parts of the electromagnetic spectrum. For example, you might have a microwave transition with a certain $\frac{\delta \nu}{\nu}$, an infrared transition, a visible transition, and an ultraviolet transition. By comparing their relative widths, $\frac{\delta \nu}{\nu}$, you are comparing them on a common, dimensionless footing. This allows for a more fundamental comparison of the "sharpness" or "Q-factor" of these different transitions, irrespective of their absolute frequencies or wavelengths. It's a very powerful unifying concept.

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Now we turn to Slide 7, titled "Kernel and Wings—Anatomy of a Spectral Line." Just like a biological specimen, a spectral line has an anatomy, different regions that have distinct characteristics and often reveal different physical processes. We broadly divide the line profile into two main parts: the kernel (or core) and the wings.

Let's first discuss the Kernel, also referred to as the core of the line.

- This is defined as the frequency interval $\nu_{1} \leq \nu \leq \nu_{2}$, where ν_{1} and ν_{2} are the two frequencies at which the intensity is half of its maximum value. So, the kernel is essentially the region encompassed by the Full Width at Half Maximum (FWHM). The width of the kernel *is* the FWHM, $\delta \nu = \nu_{2} - \nu_{1}$.

- A crucial characteristic of the kernel is that it contains half of the *maximum* intensity. This is by definition of FWHM. However, it's important to distinguish this from containing half of the *total integrated intensity* or area under the curve. The fraction of total area within the FWHM depends on the specific line shape (e.g., for a Lorentzian, about 47% of the area is within the FWHM, while for a Gaussian, it's about 76%). The statement here refers to the intensity values themselves: within this region, the intensity is at least half of the peak intensity.

- Physically, the shape and width of the kernel are typically dominated by the most probable, or strongest, physical broadening process. For example, in gases at low pressures, the kernel is often primarily determined by Doppler broadening, which arises from the thermal motion of the atoms or molecules. In other situations, like high-pressure gases or for certain transitions, collisional broadening or natural broadening might dominate the kernel.

Next, we have the Wings of the spectral line.

- The wings are the regions of the line profile that lie outside the kernel. That is, frequencies ν such that $\nu < \nu_{1}$, which is the low-frequency wing, and frequencies ν such that $\nu > \nu_{2}$, which is the high-frequency wing.
- So, if the kernel is the central, most intense part of the line, the wings are the "tails" of the distribution, where the intensity is less than half of the maximum and gradually falls off as you move further away from the line center ν_{0} .

Understanding both the kernel and the wings is essential for a complete picture of the line profile and the physics it encodes.

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Continuing our discussion on the anatomy of a spectral line, let's focus more on the characteristics and significance of the wings.

The first bullet point makes a critical observation: In the wings, the intensity falls rapidly as we move away from the line center, but theoretically, for many line shapes (like a pure Lorentzian), it never reaches *exact zero* at any finite frequency offset. Of course, experimentally, it will eventually fall below the noise floor of your detection system. More importantly, these wings, though they may be faint, carry the fingerprints of additional physical mechanisms that might be less dominant in the kernel. These can include:

- **Collisional broadening:** Even if Doppler broadening dominates the kernel, the far wings of a line in a gaseous sample are often governed by the details of interatomic or intermolecular collisions. The precise way the intensity falls off in the far wings can tell us about the interaction potentials between the colliding particles.

- **Quantum interference:** In some cases, interference effects between different transition pathways or nearby resonance states can significantly alter the shape of the wings, sometimes leading to asymmetries or characteristic dips and peaks.

So, while the kernel gives you the main story, the wings often contain the subtle subplots and finer details.

The second bullet point emphasizes that the behavior of the line profile in the wings is not just an academic curiosity; it has very practical implications and determines several important phenomena:

1. **Laser gain bandwidth:** For a laser to operate, the gain medium must provide amplification over a certain range of frequencies. The width of this gain profile is directly related to the spectral line shape of the lasing transition. The extent of the wings determines how far off-resonance the laser can still potentially lase, or how much bandwidth is available for tuning or for supporting short pulses.

2. **Radiation transport in stellar atmospheres:** When light travels through the atmosphere of a star, it is repeatedly absorbed and re-emitted by atoms and ions. The opacity of the stellar material at any given frequency depends on the line profiles of the transitions present. The wings of strong absorption lines can significantly affect the overall energy transport, as photons in the wings can travel further before being reabsorbed than photons near the line center. This is crucial for building accurate models of stellar structure and spectra.

3. **Accuracy limits of atmospheric remote sensing:** When we use spectroscopy to measure the composition of Earth's atmosphere (or other planetary atmospheres), we are often looking at absorption lines of various molecules (like CO_2 , H_2 O, O_3). The ability to accurately determine the

concentration of these species depends on how well we can model their line shapes. The wings of these absorption lines can overlap, and how they add up is critical. If the wing behavior is not correctly accounted for, it can lead to significant errors in retrieved atmospheric parameters. This is especially important for understanding greenhouse gases and climate change.

So, the wings, while perhaps less intense, are certainly not less important than the kernel.

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This slide adds a final important point regarding the wings of a spectral line, particularly in the context of modeling.

The bullet point states: "For precise modelling, wings often require different mathematical treatment (e.g., Lorentzian tails)."

This is a crucial practical consideration in quantitative spectroscopy. While a simple model (like a pure Gaussian for Doppler broadening) might adequately describe the kernel of a line, it often fails to accurately represent the far wings.

For example, Doppler broadening leads to a Gaussian profile which falls off very rapidly (exponentially with the square of the frequency offset).

However, even in a low-pressure gas where Doppler broadening dominates the core, there will always be some underlying natural broadening and potentially some collisional broadening, both of which typically contribute Lorentzian components.

Lorentzian profiles have wings that decay much more slowly (as one over the square of the frequency offset) than Gaussian profiles. Therefore, at large frequency offsets from the line center (in the far wings), the intensity predicted by a Lorentzian can be many orders of magnitude higher than that predicted by a Gaussian that fits the core well.

So, if you need to model the line profile accurately over a wide dynamic range, especially far out into the wings, you often cannot rely on a single, simple line shape function.

A common approach is to use a Voigt profile, which is a convolution of a Gaussian and a Lorentzian, as this naturally incorporates both types of behavior.

In some situations, more complex models are needed, perhaps involving sums of different profiles or modifications to account for specific physical effects like line mixing or speed-dependent collisional effects.

The mention of "Lorentzian tails" specifically highlights that even if the core appears Gaussian, the far wings are often better described by the power-law decay characteristic of a Lorentzian.

This necessity for different mathematical treatment for the wings underscores their distinct physical origin and their importance in applications where even low levels of off-resonant absorption or emission are significant, such as in atmospheric transmission calculations or in assessing crosstalk between closely spaced spectral channels. Careful attention to the wings is a hallmark of high-precision spectroscopy.

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Here we have a detailed diagram illustrating the "Anatomy of a Spectral Line: Kernel and Wings," visually summarizing what we've just discussed.

Let's examine the main graph first.

The axes are similar to the previous line profile graph: * The horizontal axis is "Frequency (\nu)". * The vertical axis is "Intensity I(\nu)". We see a bell-shaped curve representing the spectral line. * The peak intensity is at \nu_0 (nu sub zero), and its value is I(\nu_0). * The half-maximum intensity level, \frac{I(\nu_0)}{2}, is marked with a dashed horizontal line.

The graph clearly demarcates the different regions: * The central, blue-shaded region is labeled "Kernel (Core)". This region extends from \nu_1 (nu sub one) to \nu_2 (nu sub two), which are the frequencies where the intensity is \frac{I(\nu_0)}{2}. * The horizontal double arrow within this blue region is labeled "\text{FWHM} = \delta \nu = |\nu_2 - \nu_1|", explicitly showing that the Full Width at Half Maximum defines the extent of the kernel.

* The regions outside the kernel, on either side, are shaded in a light orange/pink color and labeled "Wing". * The low-frequency wing is for \nu < \nu_1. * The high-frequency wing is for \nu > \nu_2. You can see the intensity in these wing regions gradually decreases as you move further from the line center \nu_0.

Now, look at the inset graph in the upper right corner, titled "Logarithmic Intensity Scale." This is a very important addition. * The horizontal axis is still "Frequency (\nu)". The example values are 100, 500, and 900, presumably in some arbitrary units consistent with the main graph's nu-axis. * The vertical axis is now "log[Intensity I(\nu)\]", meaning the logarithm of the intensity. The tick marks are at 10^0 (which is 1, representing I_0), 10^{-1}, 10^{-2}, 10^{-3}, and 10^{-4}. This means each major division downwards represents a factor of 10 decrease in intensity.

Why is a logarithmic scale so useful? Because spectral line intensities can span many orders of magnitude. The wings of a line might be thousands or millions of times weaker than the peak. On a linear scale (like the main graph), these faint wings would be almost indistinguishable from zero. However, on a logarithmic scale, even these very low intensities become visible and their functional form can be studied.

The shape of the line profile looks different on a log scale. For example, a Lorentzian profile, which looks like a bell curve on a linear scale, would show its characteristic slow (power-law) decay in the wings more clearly as straight lines on a log-log plot, or a specific curvature on a semi-log plot like this one. A Gaussian, in contrast, would appear as a parabola on a semi-log plot (log intensity vs. frequency squared).

This inset graph powerfully illustrates why spectroscopists often plot spectra on a logarithmic intensity scale when they are interested in the behavior of the wings or in detecting weak features alongside strong ones. It allows you to see details that would be completely hidden on a linear plot. The main graph shows the overall shape and FWHM clearly, while the log plot gives a much better view of the wing structure.

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We now move to Slide 8, which provides an "Overview of Broadening Mechanisms." This serves as context for later sections where we will delve into each of these mechanisms in more detail. Understanding these mechanisms is key to interpreting the width and profile of the spectral lines we observe.

Let's go through the primary types of broadening:

1. **Natural (lifetime) broadening:**

This is a fundamental quantum mechanical effect. It arises because excited states of atoms or molecules have a finite lifetime*. An excited state doesn't last forever; it will eventually decay, typically by emitting a photon. * The Heisenberg energy-time uncertainty principle states that $\Delta E \Delta t \geq \frac{\hbar}{2}$ (Delta E Delta t is greater than or equal to h-bar over two). If an excited state has a finite lifetime Δt (often denoted by τ, tau), then there is an inherent uncertainty or spread in its energy, ΔE. * Since the frequency of the emitted photon is related to the energy difference ($\nu = \frac{\Delta E_{\text{transition}}}{h}$), this uncertainty in the energy of the excited state (and/or the ground state if it's also unstable) leads to a spread in the frequencies of the emitted photons. * This natural broadening mechanism always results in a **Lorentzian line shape**. It's an intrinsic property of the transition and cannot be eliminated, though its magnitude varies greatly between different transitions. For allowed transitions, it's often small compared to other broadening effects, but for forbidden transitions with very long lifetimes, it can be exceedingly small.

2. **Doppler (thermal motion) broadening:**

* This mechanism is due to the thermal motion of the emitting or absorbing particles (atoms, molecules, ions) in a gas. These particles are moving randomly with a distribution of velocities. * If a particle is moving towards an observer (or a detector), the light it emits or absorbs will be shifted to a higher frequency (blueshifted) due to the Doppler effect. If it's moving away, the light will be shifted to a lower frequency (redshifted). * Since the particles in a gas have a Maxwell-Boltzmann distribution of velocities along the line of sight, the observed spectral line will be a composite of all these Doppler-shifted components. * The result of this averaging over the velocity distribution is a **Gaussian line shape**. * Doppler broadening is often the dominant broadening mechanism in low-pressure gases at moderate to high temperatures. Its magnitude increases with temperature and decreases with the mass of the particle.

3. **Collisional (pressure) broadening:**

* This type of broadening arises from perturbations to the energy levels or the phase of the emitted/absorbed radiation due to collisions between the active particle and other particles in the sample (which could be other active particles or buffer gas atoms/molecules). * These collisions can interrupt the process of emission or absorption, effectively shortening the coherent interaction time, which, again via the uncertainty principle, leads to energy broadening. They can also directly shift the energy levels during the collision. * Collisional broadening typically results in a **Lorentzian line shape**. * Its magnitude is dependent on the gas pressure (hence it's also called pressure broadening), as higher pressure means more frequent collisions. It also depends on the temperature (which affects collision rates and strengths) and the nature of the colliding species.

These three – Natural, Doppler, and Collisional broadening – are often the most significant contributors to the observed linewidths in many spectroscopic experiments. We will explore them in much greater depth.

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Continuing our overview of broadening mechanisms from the previous slide:

4. Stark, Zeeman, and other field-induced broadenings:

* These types of broadening occur when the emitting or absorbing atoms or molecules are subjected to external electric fields or magnetic fields.

* **Stark broadening** refers to the effect of electric fields. Electric fields can be externally applied, or they can be microscopic fields produced by nearby ions and electrons, especially in plasmas. These fields can shift and split energy levels, leading to a broadening or splitting of the spectral line. The line shape can be complex depending on the specific quantum numbers of the states involved and the nature of the field.

* **Zeeman broadening** (or splitting) is the analogous effect for magnetic fields. Magnetic fields also lift the degeneracy of energy levels (e.g., those with different magnetic quantum numbers, m_J), causing a single line to split into multiple components. If these components are not resolved, they manifest as a broadening of the line.

* Other types of field interactions can also occur, for instance, with strong laser fields themselves (e.g., AC Stark effect or power broadening).

* The common theme is that external fields perturb the energy levels of the quantum system, thus modifying the spectral line.

5. Instrumental broadening:

* This is not a property of the atoms or molecules themselves, but rather a characteristic of the measuring apparatus – the spectrograph, spectrometer, or interferometer used to record the spectrum.

* Any real instrument has a finite resolving power. It cannot perfectly distinguish between two very closely spaced frequencies. Instead, it has an "instrumental response function" which describes how an ideal, infinitely narrow (δ function) spectral line would appear when measured by that instrument. This response function itself has a certain width.

* The observed spectrum is essentially a convolution of the true, physical line profile (due to natural, Doppler, collisional, etc., broadening) with this instrumental response function.

* Therefore, the measured linewidth will always be greater than or equal to the true physical linewidth.

To obtain the intrinsic physical line profile, the contribution from instrumental broadening must be carefully characterized and then deconvolved* from the measured spectrum. Deconvolution is a mathematical procedure that attempts to "undo" the blurring effect of the instrument. This is often a challenging but necessary step in high-resolution spectroscopy.

So, when we look at an experimental spectral line, we must remember that its observed width and shape are a combination of these intrinsic physical broadening mechanisms and the characteristics of our measurement system. Disentangling these contributions is a key task in quantitative spectroscopy. The dashes indicate the end of this overview section.

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We now move to Slide 9, which discusses "Typical Orders of Magnitude—Why Widths Matter." This slide is crucial because it puts concrete numbers to the broadening mechanisms we've just introduced, illustrating their relative importance and why understanding them is so vital for various applications.

Let's look at some examples:

First, the **Natural linewidth of a typical allowed optical transition:**

* The slide states that Γ_{nat} (Gamma sub nat, representing the natural FWHM linewidth) is approximately 10^7 Hz (ten to the power of seven Hertz). * This is equivalent to about a few Megahertz (MHz). For example, 10^7 Hz is 10 MHz. * This natural linewidth arises from the finite lifetime of the excited state due to spontaneous emission. For typical allowed electronic transitions in the visible or near-UV range, excited state lifetimes are often in the nanosecond range (e.g., 1 to 100 nanoseconds). A 10 nanosecond lifetime (10^{-8} s) corresponds roughly to a natural linewidth of about 16 MHz (using $\Gamma \approx \frac{1}{2\pi\tau}$). So, a few MHz to tens of MHz is a good ballpark figure for many common atomic and molecular transitions. While this might seem small, we'll see it can be dwarfed by other effects.

Second, the **Doppler width for the sodium D line at 300 K:**

* The sodium D line is a very famous yellow line in the spectrum of sodium, with a central wavelength λ_0 (lambda sub zero) of approximately 589 nm. * The temperature is given as 300 K, which is approximately room temperature. * Under these conditions, the Doppler width, denoted $\delta\nu_{\text{D}}$ (delta nu sub D), is approximately 1.5 GHz. That's 1.5×10^9 Hz. * Compare this to the natural linewidth: 1.5 GHz is 1500 MHz. This is about two orders of magnitude larger than a typical natural linewidth of, say, 15 MHz! This clearly shows that for many common situations (like room temperature atomic vapors), Doppler broadening can be the dominant mechanism determining the observed linewidth if you're using conventional spectroscopy.

Third, the **Collisional width in air at 1 atmosphere for the *same* transition** (presumably referring to a transition similar to the sodium D line or a generic optical transition):

* The conditions are specified: in air, at a pressure of 1 atmosphere. * We'll see the value for this on the next page, but this sets the context. Collisional broadening depends on the density of colliding partners (related to pressure) and the interaction cross-sections. At atmospheric pressure, collision rates are quite high.

These numbers immediately tell us that if we want to do spectroscopy that resolves features narrower than the Doppler width, or if we want to study the natural lineshape itself, we need techniques to either reduce Doppler broadening (like laser cooling or using atomic beams) or to circumvent it (like saturation spectroscopy or two-photon spectroscopy, which we'll cover later in the course). The sheer magnitude of Doppler broadening often masks the finer details of the natural line.

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Continuing with typical orders of magnitude for linewidths:

* We were about to see the value for the **Collisional width in air at 1 atmosphere for a typical optical transition**. The slide states that Γ_{coll} (Gamma sub coll, representing the collisional FWHM linewidth) is approximately 100 MHz. That's 10^8 Hz.

* Let's compare this to the other values. The natural linewidth was a few MHz (e.g., ~ 10 MHz). The Doppler width for sodium at 300K was ~ 1500 MHz (1.5 GHz). So, this collisional width of 100 MHz (at 1 atm) is significantly larger than the natural width but still notably smaller than the Doppler width at room temperature for a light atom like sodium.

* However, remember that collisional width is proportional to pressure. If the pressure were much higher, or if we were dealing with molecules with larger collisional cross-sections, this collisional width could become

comparable to or even exceed the Doppler width. Conversely, at very low pressures, collisional broadening becomes much less significant.

Next, the slide discusses the capabilities of **Ultra-high resolution spectrometers:**

* Examples given are Fabry-Pérot interferometers and Fourier transform interferometers (FTIRs or FTSs). These are instruments specifically designed for achieving very high spectral resolution.

These instruments can resolve spectral features, meaning they can distinguish linewidths ($\delta\nu$, delta nu), down to values less than or equal to ≤ 1 MHz under favorable conditions*.

* "Favorable conditions" means the instrument is well-aligned, stable, and the source is bright enough, etc. This 1 MHz resolution is already approaching the regime of typical natural linewidths for many allowed optical transitions. This means such instruments can begin to resolve the natural lineshape if Doppler and collisional broadening are sufficiently minimized.

Finally, the slide provides crucial **Context: laser cooling and atomic clocks.**

* Applications like laser cooling (which is used to cool atoms to microkelvin temperatures or even lower) and atomic clocks (which are the most precise timekeeping devices ever made) require spectral lines that are narrowed to the Hertz (Hz) or even sub-Hertz level!

* Compare this to the MHz and GHz figures we've been discussing. A 1 Hz linewidth is six orders of magnitude narrower than a 1 MHz natural linewidth, and nine orders of magnitude narrower than a typical Doppler width at room temperature.

Achieving such incredibly narrow lines demands the extreme suppression of all broadening sources* – natural broadening (by choosing transitions with very long lifetimes, often "forbidden" transitions), Doppler broadening (through extensive laser cooling and trapping, leading to very low atomic velocities), collisional broadening (by working in ultra-high vacuum with very dilute atomic samples), and also minimizing any field-induced broadening and instrumental effects to an extraordinary degree.

This progression of numbers – from GHz for Doppler, to tens or hundreds of MHz for collisional (at 1 atm) and natural widths, down to MHz for high-res spectrometers, and finally to Hz or sub-Hz for cutting-edge applications – really underscores why a deep understanding and control of linewidths are absolutely paramount in modern laser spectroscopy and atomic physics. The dashes indicate the conclusion of this point.

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Now we arrive at Slide 10, which addresses a practical but important question: "Why Spectroscopists Prefer Angular Frequency ω (omega)." We've touched upon this briefly before, but this slide elaborates on the reasons. Using ω (omega) instead of ν (nu) often simplifies many theoretical expressions.

The first major reason is that: **The Schrödinger equation contains the phase factor** $e^{-i\omega t}$ (e to the power of minus i omega t), making ω the natural variable in quantum dynamics.

* As we discussed earlier, the time evolution of a quantum state with energy E is governed by a phase factor $e^{-iEt/\hbar}$ (e to the power of minus i E t divided by h-bar).

* Using the fundamental relation $E = \hbar\omega$ (Energy equals h-bar times omega), this phase factor becomes $e^{-i\omega t}$.

* If we were to use ordinary frequency ν (where $E = h\nu$), the phase factor would be $e^{-i2\pi\nu t/(2\pi)}$ — no, that's not right. If $E = h\nu$, then

$$E/\hbar = \frac{h\nu}{h/(2\pi)} = 2\pi\nu.$$

So the phase factor is $e^{-i2\pi\nu t}$.

* The point is that the ω in $e^{-i\omega t}$ appears naturally when $\hbar$ is used in the denominator $(E/\hbar)$. Since the Schrödinger equation is inherently quantum mechanical and involves $\hbar$, expressions derived from it are often cleaner when angular frequency ω is used. This is because the 2π factors that would otherwise appear (linking ν to ω) are absorbed into the definition of $\hbar$ from h.

The second reason is that: **Fourier transforms and time-frequency uncertainty relations appear cleaner without extra** 2π factors.

* Fourier transforms are fundamental for relating time-domain phenomena (like the decay of an excited state or the duration of a laser pulse) to frequency-domain spectra (like the line profile or the pulse bandwidth).

* The standard definition of the Fourier transform pair often involves $e^{\pm i\omega t}$ or $e^{\pm i2\pi\nu t}$. When ω is used, the expressions for the transform and its inverse are often more symmetric and lack stray 2π factors in the exponents or prefactors.

* This cleanliness extends to the time-frequency uncertainty principle. The slide shows two forms:

* When expressed in terms of angular frequency ω and time t, one common form is:

$$\Delta\omega\, \Delta t \geq \frac{1}{2}$$

* When expressed in terms of ordinary frequency ν and time t, the same relationship becomes:

$$\Delta\nu\, \Delta t \geq \frac{1}{4\pi}$$

* Clearly, the version with $\Delta\omega$ is simpler and avoids the factor of 4π in the denominator. This is a direct consequence of $\omega = 2\pi\nu$, so $\Delta\omega = 2\pi\Delta\nu$. Substituting this into $\Delta\omega\,\Delta t \geq \frac{1}{2}$ gives $(2\pi\Delta\nu)\Delta t \geq \frac{1}{2}$, which leads to $\Delta\nu\,\Delta t \geq \frac{1}{4\pi}$.

* Since these uncertainty relations are foundational in understanding linewidths (e.g., natural broadening from lifetime) and the limits of pulse durations, using ω simplifies their statement.

These are two very compelling reasons why theoretical spectroscopists, and indeed many physicists working with waves and quantum mechanics, often prefer to work with angular frequency ω.

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Continuing with why spectroscopists often prefer angular frequency ω (omega):

A third reason is presented: **Perturbation-theory matrix elements often involve denominators containing** $\omega_0 - \omega$ (omega naught minus ω), again avoiding 2π factors.

* Perturbation theory is a cornerstone of quantum mechanics used to calculate how energy levels and transition probabilities are affected by small interactions (perturbations), such as the interaction of an atom with a light field.

* The formulae derived from perturbation theory frequently include terms in the denominator that look like $\left(E_{\text{initial}} - E_{\text{intermediate}} \pm \hbar\omega_{\text{photon}}\right)$ or, when expressed in frequencies, $\left(\omega_{\text{transition}} - \omega_{\text{light}}\right)$ or $\left(\omega_{\text{resonant}} - \omega_{\text{applied}}\right)$.

* If these were written in terms of ordinary frequency ν (nu), they would often look like $h\left(\nu_{\text{resonant}} - \nu_{\text{applied}}\right)$ or $\left(\nu_{\text{resonant}} - \nu_{\text{applied}}\right)$, but if they arise from energy differences involving $\hbar\omega$, then using ω directly avoids having to write $\hbar\left(2\pi\nu_{\text{resonant}} - 2\pi\nu_{\text{applied}}\right)$ and then factoring out the 2π.

* Essentially, because energy in quantum mechanics is naturally linked to $\hbar\omega$, differences in such energies or comparisons with photon energies (also $\hbar\omega$) are simpler when expressed directly in ω.

Now, having made the case for ω, the slide offers a practical perspective: **In plotting, spectroscopists may stick to** ν (Hz) for an intuitive frequency scale, but algebraic derivations almost always adopt ω.

* This is a very common practice. When presenting experimental data or discussing frequencies in a way that needs to be easily related to instrument settings or common wavelength ranges, units of Hertz (Hz, MHz, GHz, THz) or wavenumbers (cm^{-1}) are often more intuitive for experimentalists.

* However, when developing the underlying theory, deriving equations for line shapes, transition rates, or nonlinear optical susceptibilities, the mathematical elegance and compactness offered by ω usually make it the preferred choice. Most theoretical textbooks and papers in spectroscopy will use ω extensively in their derivations.

Finally, a crucial reminder: **Conversion is straightforward; always keep track of units (**rad s^{-1} vs. Hz).

* The relationship is simple: $\omega = 2\pi\nu$.

* It's vital to be clear about which type of frequency is being used, especially when plugging numbers into formulas or comparing theoretical expressions with experimental results. The units are your guide: * ω (omega) has units of radians per second (rad s^{-1}), or often just s^{-1} since radians are dimensionless. * ν (nu) has units of Hertz (Hz), which is also s^{-1} but specifically means cycles per second.

* Mistaking one for the other will lead to errors by a factor of 2π, which is about 6.28 – a significant discrepancy! So, always be meticulous about units and the definitions of frequency being used.

The dashes indicate the end of this discussion on frequency units. This concludes our initial overview of spectral line characteristics and the reasons behind the conventions used in the field. We are now well-prepared to delve deeper into the specific broadening mechanisms.