

[Review for the Analytical Test](#)- About 50 questions are provided to help you review for a graduate school entrance exam.

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Related URL's:

[Society for Applied Spectroscopy](#)

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**This is an intended review of Instrumental Analysis to help prepare you for the Analytical test -- Good luck Chris and Kevin!**

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**[Instrumental: Part One](#)**

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**[Instrumental: Part Two](#)**

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**[Instrumental: Part Three](#)**

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**[Instrumental: Part Four](#)**

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**[Instrumental: Part Five](#)**

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A \_\_\_\_\_ converts one type of energy to another, an example of which is the conversion of a voltage signal to a mechanical signal for ultrasonic analysis.

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A [random/systematic](#) error is always off by a certain amount and is thus difficult to notice, but a [random/systematic](#) error fluctuates around the correct value, and you can work around it by taking several readings and calculating an average.

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Glance at page 21, Fig. 2-13: There could be a simple question "what math operation is this operational amplifier good for?" Notice that the a) b) and d) op-amps are the same except for the part that comes before the S junction. Notice that integration is the only op-amp with a capacitor in the feedback loop.

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Convert this binary number [101010](#) to a decimal number.

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[What](#) causes thermal noise or Johnson noise?

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[What](#) causes shot noise?

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With regard to the signal to noise ratio, what is the [improvement](#) if you double the number of data points taken?

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The [visible spectrum](#) runs from what to what (in nanometers?)

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The typical Infrared spectra [ranges](#) from what to what (in reciprocal centimeters?)

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Correlate the phenomenon listed below with the types of spectroscopy listed even further below:

core electron ejection (also called inner electrons)

valence electron excitation (bonding electrons)

rotation of molecules

rotation and vibration of molecules

effect on the spin of nuclei in a magnetic field

[Electron Spectroscopy for Chemical Analysis](#)

[Infrared Absorption and Raman Scattering](#)

[Microwave absorption](#)

[X-ray Absorption, emission, fluorescence, and diffraction](#)

[Ultraviolet absorption, emission, and fluorescence](#)

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Does energy [decrease/increase](#) as one travels along the infrared spectrum from 4000 reciprocal centimeters ( $\text{cm}^{-1}$ ) to 450 reciprocal centimeters ( $\text{cm}^{-1}$ ); said another way, the magnitude of the

numbers is decreasing?

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For a beam of light, [amplitude/frequency](#) corresponds to power or intensity, and [amplitude/frequency](#) corresponds to energy.

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i Refractive index is a measure of the interaction of a medium with light: what is the [formula](#) that relates the speed of light to refractive index?

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# transducer

# **systematic**

**random**





**the thermal agitation of electrons or other charge carriers in resistors, capacitors, radiation detectors, electrochemical cells, and other resistive elements in an instrument.**

**Shot noise is encountered when a current involves the movement of electrons or other charged particles across a junction.**

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**It could be a junction found at the p and n interfaces of an electric circuit.**

**the improvement is 1.41 (the square root of two) because the signal to noise ratio (the higher this ratio, the better) is proportional to the square root of the number of data points taken.**

**400 nm (purple) to 700 nm (red)**

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**Green is around 510 nm, and has been sited on previous tests.**

## **4000 cm<sup>-1</sup> to 450 cm<sup>-1</sup>**

## **decrease**

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**Decreasing numbers mean decreasing energy. Increasing wavelength corresponds to decreasing energy, and since reciprocal wavelength is inversely proportional to wavelength, decreasing wavenumbers corresponds to increasing wavelength.**

# amplitude

# frequency



the refractive index is the speed of light divided by the velocity of the radiation in the medium

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By the way, don't take this to mean that the speed of light slows down as light travels through a medium; light travels at the speed of light from molecule to molecule for for different material the density is different and the time a photon is trapped by an atom before reemission varies.

What causes [Rayleigh scattering](#)?

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What is [Raman scattering](#)?

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What is [the most common source](#) for ultraviolet radiation?

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What does the [Fourier Transform](#) achieve?

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What is the [mathematical relationship](#) between absorbance and transmittance?

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Use an [equation](#) to relate the following terms: absorbance, molar absorptivity coefficient, solution concentration, and pathlength.

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A graph of absorbance vs. concentration is linear but as concentration is increased, a point is reached where the function departs from linearity (the first derivative changes from a constant to a decreasing function). [Why](#)?

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[Why](#) must a deuterium lamp used for a ultraviolet source be constructed from quartz rather than glass?

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***"Forbidden Is Not Forever..."*** was a quote by a physicist with regard to a class of transitions called forbidden transitions which actually occur, but with probabilities which are less than [what number](#)?

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[How](#) does fluorescence differ from phosphorescence?

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**Rayleigh scattering is scattering caused by molecules or aggregates of molecules ("chunks") with dimensions significantly smaller than the wavelength of radiation**

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**Rayleigh scattering makes the sky blue because shorter wavelengths are scattered more than longer wavelengths (there is a wavelength dependence.)**

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**Raman scattering occurs when the atom which absorbed the photon undergoes vibrational-rotational changes before emitting a photon of a different frequency.**

## **A deuterium (D<sub>2</sub>) lamp**

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**deuterium is the isotope of hydrogen with two neutrons**

**the fourier transform is a "superoperator", a mathematical technique, that which takes a *time domain graph* of changes in radiant power with time, and converts it to the *frequency domain spectrograph*, which we are used to (e. g. nm for UV-Vis and  $\text{cm}^{-1}$  for IR.)**

**absorbance (the common log of incident power divided by the power that exits the test sample) is the negative of the common log of transmittance.**

**A = (epsilon) b c**

**A is absorbance, b is cell path length, and c is the solution concentration**

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**But of course, the units of epsilon must agree with the units of b and c and absorbance has no units**



**the average distance between the solute molecules which are absorbing the light decreases to the point where they start effecting each others charge distributions.**

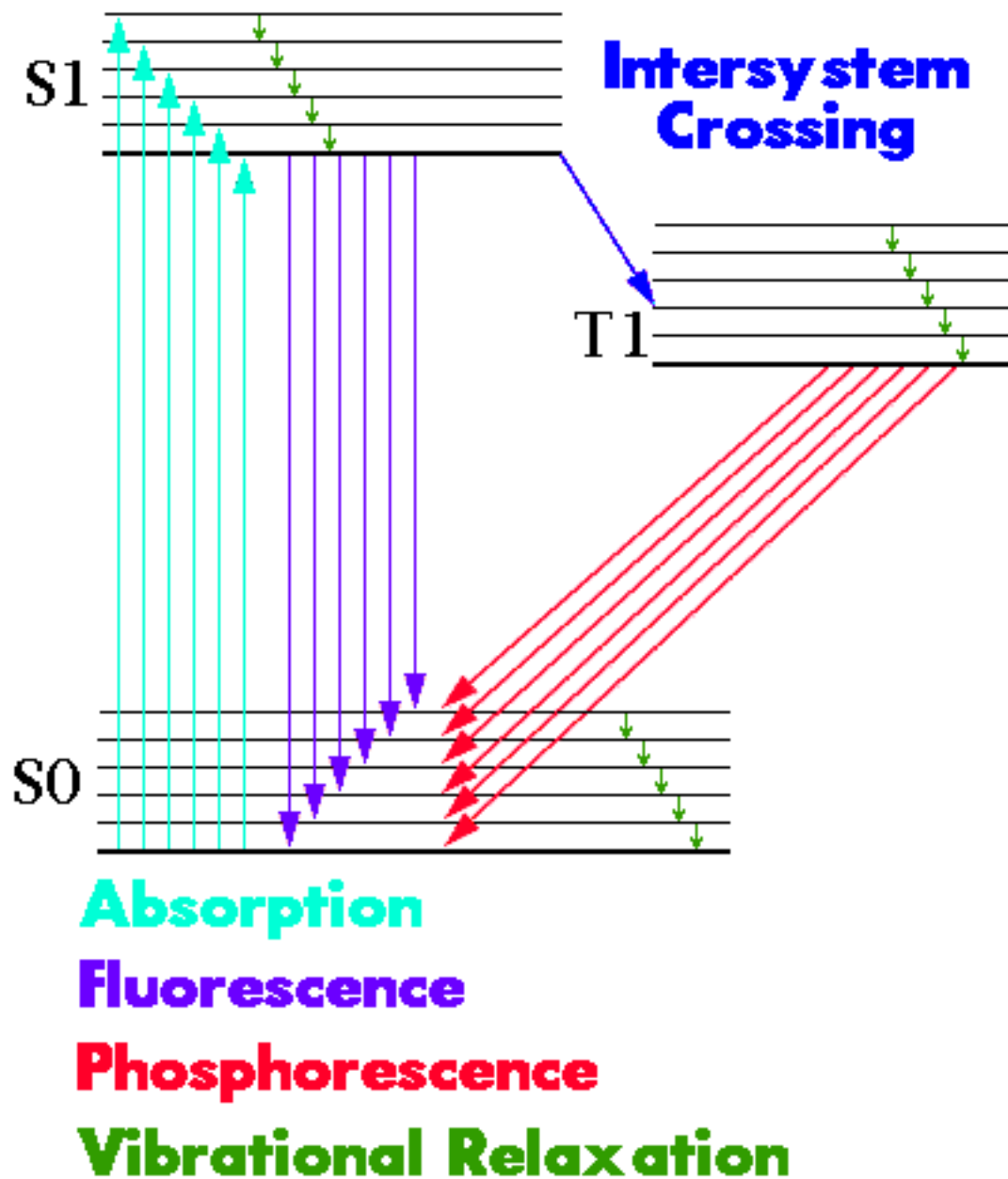
**glass absorbs strongly below 350 nm.**

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**0.01**

**Fluorescence does not involve a change in electron spin, but phosphorescence does.**

How does the [sensitivity](#) of luminescence methods compare to absorption methods? (the term luminescence encompasses both fluorescence and phosphorescence.)



**S0** is the ground singlet state  
**S1** is the first excited singlet state  
**T1** is the first excited triplet state

What are the time frames for the following quantum events?

[Absorption](#)

[Fluorescence](#)

## [Phosphorescence](#)

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The time required for fluorescence emission is so long [because ...](#)

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What is the [lifetime of a vibrational state](#)? Said another way, if a molecule is not in the lowest vibrational mode for a given state, such that it can undergo a vibrational mode (and still stay in the same state), how long before the vibrational change (purple on the above figure) occurs?

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Fluorescence is favored by to what extent a molecule is [flexible/rigid](#).

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The quantum efficiency of fluorescence (the percentage of absorbed photons which are reemitted by fluorescence) improves with [decreasing/increasing](#) temperature.

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The process of taking a solution and converting it to a mist of finely divided droplets by a jet of compressed air is call [\\_\\_\\_\\_\\_](#).

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What is [the famous name](#) given to the two wavelengths 589.0 nm and 589.6 nm?

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What is [Doppler broadening](#)?

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What is [Pressure broadening](#)?

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**detection limits are often one to three orders of magnitude (10-fold to 1000-fold) smaller; this places detection limits in the parts-per-billion range**

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**later on there should be a question that says phosphorescence is even more sensitive than fluorescence**

**$10^{-14}$  to  $10^{-15}$  seconds, or 1 to 10 femtoseconds**



## **$10^{-5}$ to $10^{-9}$ seconds**

**T1 to S0 transition involves a forbidden transition from a triplet state (T1) to a singlet state (S0.)**

**rigid**

## **decreasing**

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**As the temperature drops there are fewer and fewer molecular collisions per unit time which can cause a loss of energy through external conversion.**

## The Sodium D Line

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**At first scientists could only see one yellow line. Refractive index measurements of liquids are often recorded at the wavelength 489 nm, with the letter 'D' indicating "sodium D line."**

**Because the atoms are moving, and their movement changes while they are in the excited state (or possibly due to the absorption of the incident radiation), atoms which experience an increase in the velocity component toward the detector will emit radiation of a higher energy (shorter wavelength) than the incident radiation, and atoms which experience a decrease in the velocity component toward the detector will emit radiation of a lower energy (longer wavelength) than the incident radiation.**

**As the pressure increases, there more collisions occur between the absorption of the incident radiation, and the emission of radiation, and the changes in energy from these collisions becomes more pronounced.**

What [information](#) does the Boltzmann Equation bring together?

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Raman spectroscopy is often called a complimentary technique to infrared spectroscopy because it works in the same wavelength region, but it can do things that infrared can't (and vice verse.) [Name some](#). Right now there are three in the answer.

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In Raman spectroscopy, Stokes lines have [larger/smaller](#) wavenumbers than Rayleigh lines.

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Raman shifts [decrease with/increase with/are independent of](#) an increase in the wavelength of excitation.

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It is best to use a \_\_\_\_\_ as the excitation source for Raman spectroscopy because the quantum efficiency of the Raman transitions is so low.

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Anti-Stokes lines have an appreciably [greater/lesser](#) intensity than the corresponding Stokes lines.

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Fluorescence may interfere with [anti-Stokes shifts/Stokes shifts](#) but not with [anti-Stokes shifts/Stokes shifts](#).

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For an infrared transition to occur, the molecule of interest must \_\_\_\_\_.

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For a raman transition to occur, the molecule of interest must \_\_\_\_\_.

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<http://1-40a.html>>Compare dc plasma jet sensitivity to inductively coupled plasma jet sensitivity.

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The above is a figure of attenuated total reflectance. Notice that the light bounces back forth in the sell. The idea is the principle of Snells law: the reflection occurs because the beam of radiation is passing [less dense to a more dense/more dense to a less dense](#) medium. Also [decreasing/increasing](#) the angle of the incident beam of radiation increases the fraction of radiation that is reflected.

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**The Boltzmann equation relates the number of atoms in state  $i$  to the number of atoms in state  $j$  to 1) the difference in energy between the two states  $i$  and  $j$ , 2) temperature, in Kelvin, of course, and 3) to the ratio of  $P(i)$  to  $P(j)$ .**

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**If  $i$  is an excited state, and  $i$  is triply degenerate, and  $j$  is a lower state, and  $j$  is a singlet, the  $P(i)$  over  $P(j)$  will be the factor 3.**

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**This has been sited on the P-Chem test.**

- 1. Water is "Raman invisible" so Raman spectra can be taken from aqueous solutions.**
- 2. Glass or quartz cells can be used, whereas for infrared you have to use sodium chloride or some other atmospherically unstable windows (which have to be stored in a dry dessicator to protect them from the water in Earth's atmosphere.)**
- 3. Raman selection rules are more selective (fewer transitions are allowed) so the spectrum is not nearly as likely to be as "cluttered" (loaded with many overlapping peaks) as will be the case for an infrared spectrum. [This is a problem if Raman selection rules do no allow appreciable absorption for the molecule of interest.]**

**Stokes lines are found at wavenumbers that are smaller than the wavenumber for the Rayleigh peak. And Anti-stokes lines are found at wavenumbers that are larger than the wavenumber for the Rayleigh peak.**

## **Fluorescence may interfere with Stokes shifts**

## **possess a permanent dipole moment**

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**Skoog said "Infrared absorption requires that a vibrational mode of the molecule have a change in the dipole or charge distribution associated with it"; what I put at the top is the more common short definition.**

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**Diatomic molecules such as oxygen, nitrogen, and chlorine, are not infrared active because both the ground state molecules and the "stretched" excited state molecules have no net dipole.**

**be polarizable (it is probably more accurate to say "it must have a bond that is polarizable.)**

**1700 cm<sup>-1</sup>**

What is the famous [IR vibrational stretch frequency](#) of the carbonyl peak? (C=O)

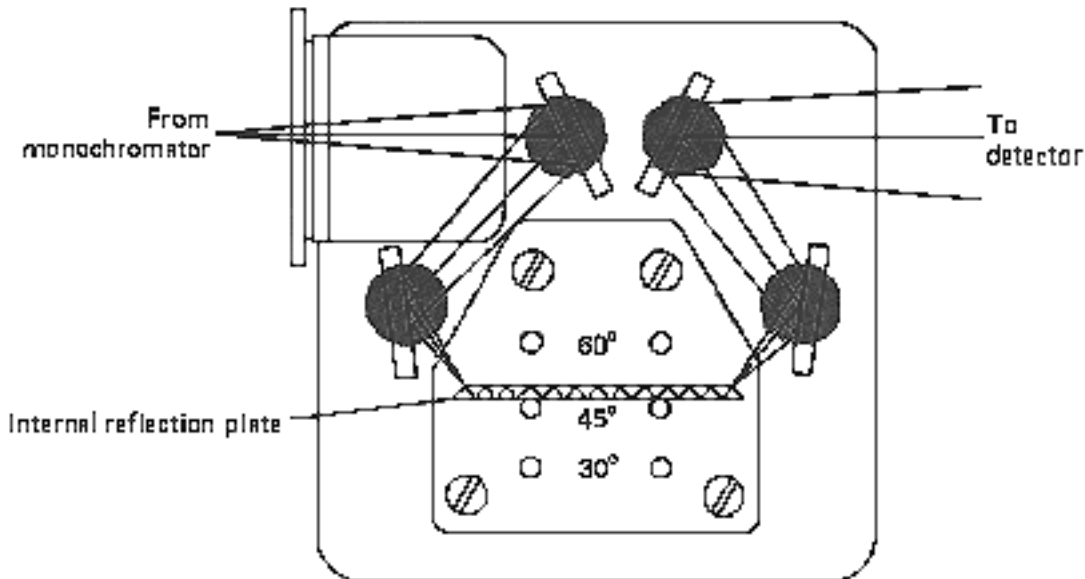
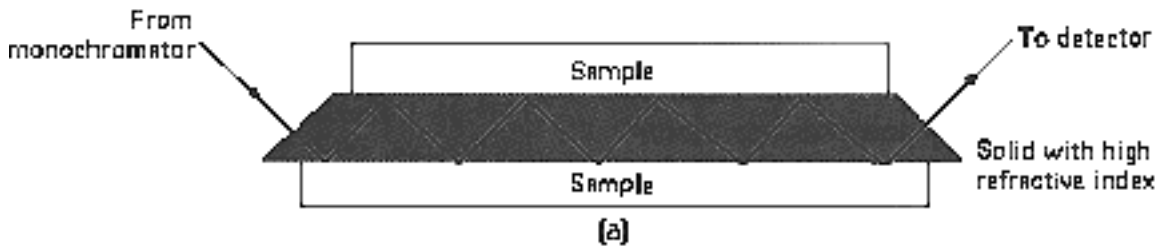
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What is the [number of vibrations](#) for a linear molecule?

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What is the [most common source](#) for atomic absorption measurements?

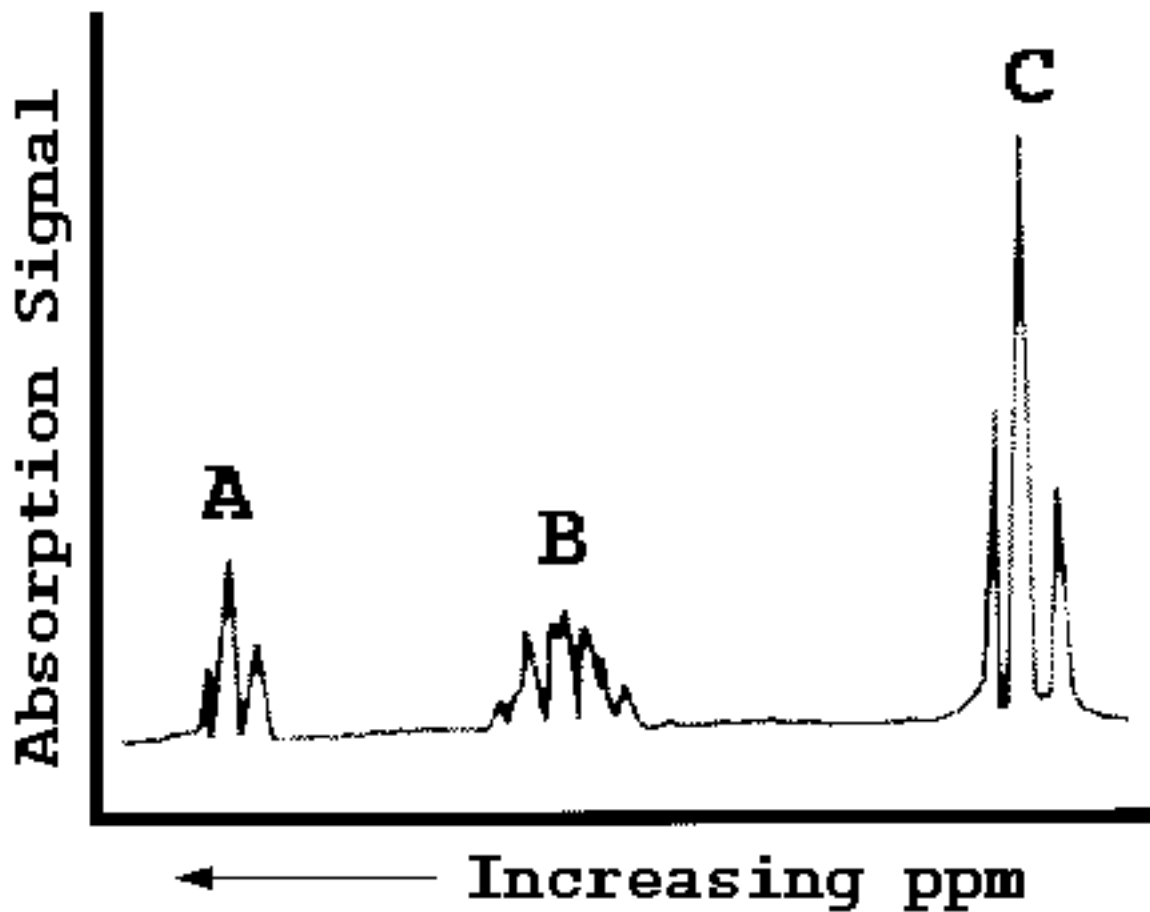
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Ethanol has

[how many](#) different types of hydrogens (that is to say, hydrogens which "feel" different chemical environments?) [Assign](#) the hydrogens to the peaks shown in the above figure.

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**(3N - 5)**

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**N is the number of atoms in the molecule**

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**For a nonlinear molecule, the answer is (3N - 6)**

## **A hollow cathode lamp**

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**A hollow cathode lamp consists of a tungsten anode and a cylindrical cathode sealed in a glass tube that is filled with neon or argon at a pressure of 1 to 5 torr. the cathode is constructed of the metal whose spectrum is desired or serves to support a layer of that metal.**

## **from a more dense to a less dense medium**

**increasing**

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**Above a certain angle, known as the critical angle, reflection is complete.**