

## 1: USA1 - Method for the laser spectroscopy of gases - Google Patents

*Many of the modern spectroscopic methods involve one or several lasers and are then called laser spectroscopy. Due to the enormous potentials of lasers in terms of temporal and spatial coherence, narrow linewidth and wavelength tunability, optical power (particularly peak power), ultrashort pulse generation etc., the field of spectroscopy.*

The invention also relates to a spectrometer for the carrying out of such a method. It is known for the examination of a gas sample as to its composition and in particular as to the concentration of a specific gas of the sample to derive this information using spectroscopy with reference to the specific absorption of radiation such as light through different gases or gas mixtures. Laser spectrometers are typically used for this purpose in which the light of a laser is irradiated through the sample which is, for example, located in a measurement space, for instance a measurement cell, or is conducted through a measurement space. A conclusion can be drawn on the concentration of a gas or its portion in the sample from the comparison of an absorption spectrum obtained in this manner using spectra known for different gases. Different gases have different typical wavelengths at which they have especially high absorption. The corresponding maxima in the absorption spectrum which correspond to minima in the transmission spectrum are ideally sharp absorption lines. Due to the blur relationship, to the pressure of the gas and to the temperature dependent Doppler effect, real absorption lines are, however, widened to form a specific absorption line shape. As a rule, it substantially has a Voigt profile which results on the folding of a Gaussian curve which is typical for a temperature dependent Doppler broadening with a Lorentz curve whose width is typically pressure dependent. A whole wavelength range is therefore examined for the measurement of one or more such absorption lines in an absorption spectrum in that the laser of the spectrometer, for example, runs through a linear wavelength ramp. In this respect, the linear ramp can also be part of a saw tooth function or of a triangle function to run through the same wavelength range a plurality of times. The wavelength range is selected such that one or more absorption lines of the gas to be examined are covered by it. An extension of this direct spectroscopy is represented by wavelength modulation spectroscopy in which the substantially continuous running through of the wavelength range is overlaid by a modulation of the wavelength which is fast with respect to it. This wavelength modulation is typically sinusoidal with a fixedly predefined modulation frequency. The wavelength modulation can, however, differ from a harmonic extent since a real laser as a rule does not perfectly convert the modulation, predefined, for example, as a modulated current signal or voltage signal, into a modulation of the wavelength. Since the absorption spectrum acts as a transfer function, the wavelength modulation of the laser light is converted by the sample due to the absorption into a correspondingly modulated absorption signal which is recorded by the spectrometer. The portions at the modulation frequency and at whole-number multiples of the modulation frequency are determined from the modulated absorption signal for the evaluation. This can take place, for example using phase-sensitive amplifiers, typically lock-in amplifiers, or by calculation processing, for instance by means of a Fourier analysis. The signals thus determined, which indicate the portion of the modulated absorption signal at the modulation frequency or at a multiple of the modulation frequency for every wavelength, are also called derivative signals since they substantially, i. The portion at the modulation frequency itself in this respect corresponds to the first derivation and is also called a  $1f$  signal; the portion at double the modulation frequency is called a  $2f$  signal and corresponds to the second derivation, etc. On the basis of this relationship, the derivative signals substantially contain the same information which is also contained in the direct absorption signal so that the gas concentration or the sample composition can also be determined from a respective derivative signal. The advantage of the use of the derivative signals is in this respect that the information to be determined can be displaced into higher frequency ranges in which the signal to noise ratio is as a rule better than in low frequency ranges. In addition, background signals which falsify the absorption spectrum as base lines to be deducted can be partly eliminated by the derivative signals. For example, the influence of a constant offset is eliminated in the  $1f$  signal; in the  $2f$  signal the influence of any desired linear base lines, etc. The higher the degree of the derivative signal, the more complex base lines are filtered from the signal, but the lower the

signal intensity becomes. For this reason, the 2f signal is typically used as a good compromise between the advantages and disadvantages of higher derivations for the evaluation. A method for gas analysis using laser spectroscopy according to the principle of wavelength modulation spectroscopy is described in EP 1 A2. It is in particular represented therein how, as part of the signal evaluation, conclusions can be drawn on parameters such as the concentration of a gas from the 2f signal of an absorption spectrum. It is furthermore described that, on the determination of the gas concentration, variable conditions, for example changes of state variables of the gas such as pressure, temperature and external gas influences, can be taken into account which are determined as part of a calibration. Such a calibration can be very complex since the respective falsifying influence of as many combinations of the variable parameters as possible on the measured gas concentration value has to be determined for as many such combinations which can be considered as possible. In addition, the extent of the falsification, in particular for parameters which relates to device properties, can vary over time so that the calibration has to be repeated at regular intervals to adapt to the changed influences. The measured gas concentration value can, however, not only depend on the gas concentration itself and on the named falsifying influences, but in particular also on the selected wavelength modulation. It is therefore known to adapt the amplitude of the wavelength modulation such that falsifying influences, in particular of the pressure of the gas, on the measured gas concentration value are already compensated on the measurement and not only as part of a downstream evaluation. For a specific pressure range as part of a calibration, EP 2 A1, for example, proposes determining and subsequently using in the measurement that amplitude of the wavelength modulation at which the influence of the pressure on the measured gas concentration value is so small that it can essentially be neglected. The amplitude is in this respect changed just such that the influence of the pressure on the measured gas concentration value is compensated. These methods are, however, comparatively complex to the extent that a separate calibration process has to be carried out for determining the modulation amplitude or the spectrometer has to comprise a pressure sensor for determining the pressure of the sample. This object is satisfied by a method having the features of claim 1. The object is correspondingly satisfied by a spectrometer which is adapted to carry out the method in accordance with the invention. Preferred further developments are the subject of dependent claims. The measured gas concentration values are measured values which reflect the concentration of the gas. The determination of the gas concentration can in this respect mean the determination of the gas concentration in a sample, which term should also include the determination of the concentration of a gas component in a gas or the determination of the composition of a gas. The first measured gas concentration value and the second measured gas concentration value can be derived in the same manner or in a different manner from the first or second derivative signals respectively. For example, the first and the second measured gas concentration values can be a level, a spacing, a width or an area of the respective derivative signal or the first measured gas concentration value can be the first derivative signal and the second measured gas concentration value can be the second derivative signal. In the method in accordance with the invention, it is therefore not the state variable of the gas which has a falsifying effect on the measured gas concentration value which is directly monitored to adapt the wavelength modulation to a change in the state variable. The adaptation of the wavelength modulation rather takes place with respect to changes in the absorption signal which have an effect on the first and the second derivative signals and, derived from this, on the first and second measured gas concentration values. For this reason, the state variable does not have to be detected by means of a separate sensor. Finally, the adaptation of the wavelength modulation also takes place in response to a change of the state variable in the method in accordance with the invention. However, this change is determined with reference to the anyway measured absorption signal—namely via the ratio of two measured gas concentration values which are derived from derivative signals of the absorption signal—and not by a separate measurement of the state variable. The named ratio in this respect replaces the state variable as the regulation value for the adaptation. The adaptation of the wavelength modulation can in particular take place continuously, that is in the sense of a continuous regulation. Accordingly, the respectively present actual value of the ratio between the first and the second measured gas concentration values is continuously compared with a ratio predefined as the desired value. On a deviation of the actual value from the desired value, the wavelength modulation is adapted according to known

regulation principles such that the correction counters the deviation in order to compensate the deviation as largely as possible. In this manner, the actual ratio is kept substantially constant at the predefined desired value. It is in particular utilized in the method in accordance with the invention that a change in the state variable of the gas can have a different effect on two different derivative signals of the same absorption signal. The influence of the state variable on the measurement can therefore be derived by a combined observation of the information from two different derivative signals the first derivative signal and the second derivative signal. This combined observation actually takes place by the forming of the ratio. The adaptation of the wavelength modulation can comprise different adaptations and take place in different manners. The adaptation of the wavelength modulation is in particular an adaptation of its amplitude. Alternatively or additionally, the frequency of the wavelength modulation can also be adapted. The wavelength modulation can be continuously optimized by the method in accordance with the invention despite absorption line shapes variable in dependence on state variables of the gas. This optimization of the wavelength modulation has the additional advantage that a calibration of the measurement to the actual properties of the radiation source, e. The radiation source can namely admittedly have differences from default values with respect to the actually transmitted radiation. These differences can, however, largely be compensated within the framework of the method in accordance with the invention. In this respect, the norming can in particular take place proportionally to the intensity. The intensity can, for example, be measured as a portion of the absorption signal or separately therefrom as the intensity of the radiation received, for instance, by means of the detector of a spectrometer. If the state variable comprises at least the pressure of the gas, a pressure sensor for determining the pressure of the gas for a subsequent pressure correction of the measured data can advantageously be dispensed with. If the state variable comprises at least one external gas influence of the gas, the broadening of the absorption signal due to any unknown external gas portions in the examined sample also does not need to be taken into account separately in the evaluation of the measurement. The level of an extreme can, for example, be the level of a central maximum in an absorption wavelength of the gas. If the respective derivative signal is a derivative signal which corresponds to an even-number derivation of the absorption signal  $2f$ ,  $4f$ , etc. The value-based spacing of the central maximum from one of the two minima or from an average value of the two minima can be used as the named spacing. Derivative signals which correspond to odd-number derivations of the absorption signal  $1f$ ,  $3f$ , etc. In this case, the value-based spacing of this maximum and of this minimum can be used for the determination of the named area. The named width is preferably a full width at half maximum of an extreme of the respective derivative signal or a spacing between two extremes, between two zero crossings or between one extreme and one zero crossing of this derivative signal. Substantially all pronounced and clearly identifiable points of the derivative signal can therefore be used for determining the width which make it possible to determine the degree by which the absorption line is broadened by different possible influences. An area of the respective derivative signal is, for example, an area enclosed between the x axis and the derivative signal, with the area being able to be restricted, for example, to a wavelength range between two zero crossings and with area portions beneath the x axis being able to be deducted from area portions above the x axis or to be added to them. It is furthermore advantageous if the ratio to be kept substantially constant is fixed in dependence on a pressure range of the gas. For example, the ratio pressures to be kept constant for comparatively high can be fixed to a first value and for comparatively low pressures to a second value from which a selection can be made. Finer gradations up to a continuous connection between the ratio and the pressure range are, however, also possible. The pressure range can in this respect be predefined from external or estimated. In this respect, it is not a question of measuring the exact pressure, but rather of only determining a range in which the actual pressure lies with at least some probability. Even if in general different ratios could be used as a regulating value independently of a respective pressure range, some ratios may be more suitable than others to compensate the influence of the state variable in this pressure range in dependence on the pressure range. The ratio to be kept substantially constant is preferably fixed such that the first measured gas concentration value entering into this ratio is substantially at a maximum. In general, the aim of compensating the influence of the at least one state variable on the measurement in the measurement data by adapting the wavelength modulation can be achieved using

different ratios than the respective desired value of a regulation. It is, however, advantageous to keep such a ratio constant at which at least one of the measured gas concentration values is particularly large, in particular in the pressure range to be expected. In this manner, at least this measured gas concentration value has a particularly good signal to noise ratio, whereas the signal to noise ratio of the other measured gas concentration value can be worse. Since a simultaneous optimization of the signal to noise ratio of the first and second measured gas concentration values is not generally possible, the ratio to be kept constant is selected in accordance with this further development such that at least one measured gas concentration value becomes maximum and therefore has an optimized signal to noise ratio. The regulation to a constant ratio is substantially not thereby negatively influenced that a measured gas concentration value is directly noise-optimized, whereas it is accepted that the other measured gas concentration value has a worse signal to noise ratio. In a conventional process, this calibration function would represent the only compensation of falsifying influences on the measurement. The calibration function would in particular also take account of the influences of at least that one state variable whose influence is eliminated in the first measured gas concentration value due to the method in accordance with the invention. On a use of the method in accordance with the invention, the calibration function therefore advantageously only has to compensate a smaller number of falsifying influences and can therefore be substantially less complex than a conventional calibration function. The calibration function can, for example, be a function of the state variables of the gas to be taken into account. The more state variables which have to be taken into account, the more dimensions the calibration function has. The dimensionality of the calibration function can, however, be reduced by the method in accordance with the invention. For example, instead of a calibration function which takes account of the pressure, an external gas influence and the temperature of the gas, a calibration function can be provided in which only the temperature has to be taken into account. Whereas for the determination of a calibration function, which takes account of the pressure, the external gas influence and the temperature complex, test measurements have to be carried out at different pressures, external gas influences and temperatures, a calibration function which only takes the temperature into account can also be determined by calculation since the temperature relationship is a purely physical, known relationship. The further calibration of the measured data is thus also simplified by the method in accordance with the invention. Instead of an area or of a hyperarea in a multidimensional space, the calibration function can be. Since the calibration function is moreover fixed in dependence on the ratio to be kept substantially constant, the calibration function is particularly well suited to compensate just those falsifying portions of the measurement signal which are not compensated by the ratio kept constant. Corresponding calibration functions can in particular already be determined for different ratios prior to a respective measurement.

## 2: Laser-induced breakdown spectroscopy - Wikipedia

*The Fritz Haber Symposium on Methods of Laser Spectroscopy was held in Ein Bokek, Israel, on the shores of the Dead Sea, on December , The location is the lowest place on earth, meters below sea level.*

Attosecond-to-picosecond spectroscopy[ edit ] Dynamics on the as to fs time scale is in general too fast to be measured electronically. Most measurements are done by employing a sequence of ultrashort light pulses to initiate a process and record its dynamics. The width of the light pulses have to be on the same scale as the dynamics that is to be measured. Ti-sapphire laser systems use Ti-sapphire as a gain medium. The pulses will go into a stretcher where the pulse duration is stretched, and then to a regenerate amplifier, where the pulse energy is amplified. The output pulses from the regenerate amplifier are further sent to a multi-pass amplifier, where the pulses can be amplified to even higher energies. The pulses from either the regenerate amplifier or the multi-pass amplifier are sent to a compressor, where the pulse duration is compressed. Dye laser[ edit ] A dye laser is a four-level laser which uses organic dye as the gain medium. Pumped by a laser with a fixed wavelength, due to various dye types you use, different dye lasers can emit beams with different wavelengths. A ring laser design is most often used in a dye laser system. Also, tuning elements, such as a diffraction grating or prism, are usually incorporated in the cavity. This allows only light in a very narrow frequency range to resonate in the cavity and be emitted as laser emission. Fiber laser[ edit ] A fiber laser is usually generated first from a laser diode. The laser diode then couples the light into a fiber where it will be confined. Different wavelengths can be achieved with the use of doped fiber. The pump light from the laser diode will excite a state in the doped fiber which can then drop in energy causing a specific wavelength to be emitted. This wavelength may be different from that of the pump light and more useful for a particular experiment. X-ray generation[ edit ] Ultrafast optical pulses can be used to generate x-ray pulses in multiple ways. An optical pulse can excite an electron pulse via the photoelectric effect , and acceleration across a high potential gives the electrons kinetic energy. When the electrons hit a target they generate both characteristic x-rays and bremsstrahlung. A second method is via laser induced plasma. When very high intensity laser light is incident on a target, it strips electrons off the target creating a negatively charged plasma cloud. The strong Coulomb force due to the ionized material in the center of the cloud quickly accelerates the electrons back to towards the nuclei left behind. Upon collision with the nuclei, Bremsstrahlung and characteristic emission x-rays are given off. This method of x-ray generation scatters photons in all directions, but also generates picosecond x-ray pulses. Conversion and characterization[ edit ] Pulse characterization[ edit ] In order for accurate spectroscopic measurements to be made, several characteristics of the laser pulse need to be known; pulse duration, pulse energy, spectral phase and spectral shape are among some of these. Methods allowing for complete characterization of pulses include frequency-resolved optical gating FROG and spectral phase interferometry for direct electric-field reconstruction SPIDER. It will not change the duration or phase of the pulse during the amplification. Pulse compression shorten the pulse duration is achieved by first chirping the pulse in a nonlinear material and broadening the spectrum, with a following compressor for chirp compensation. Fiber compressor is generally used in this case. Pulse shapers usually refer to optical modulators which applies Fourier transforms to laser beam. Depending on which property of light is controlled, modulators are called intensity modulators, phase modulators, polarization modulators, spatial light modulators. Depending on the modulation mechanism, optical modulators are divided into Acoustic-optic modulators, Electro-optic modulators, Liquid crystal modulators etc. Each is dedicated into different applications. It was first observed in by McPherson et al. It is realizable on a laboratory scale table-top systems as opposed to large free electron-laser facilities. High harmonic generation in atoms is well understood in terms of the three-step model ionization, propagation, and recombination. The intense laser field modifies the Coulomb potential of the atom, electron tunnels through the barrier and ionize. The free electron accelerates in the laser field and gains momentum. When the field reverses, the electron is accelerated back toward the ionic parent and releases a photon with very high energy. For this reason frequency conversion techniques are commonly used to extend the operational spectrum of existing laser light sources. The most

widespread conversion techniques rely on using crystals with second order non linearity to perform either parametric amplification or frequency mixing. Frequency mixing works by superimposing two beams of equal or different wavelengths to generate a signal which is a higher harmonic or the sum frequency of the first two. Parametric amplification overlaps a weak probe beam with a higher energy pump beam in a non linear crystal such that the weak beam gets amplified and the remaining energy goes out as a new beam called the idler. This approach has the capability of generating output pulses that are shorter than the input ones. Different schemes of this approach have been implemented. A probing light source, typically a xenon arc lamp , is used to obtain an absorption spectrum of the compound at various times following its excitation. As the excited molecules absorb the probe light, they are further excited to even higher states. After passing through the sample, the unabsorbed light from the arc lamp continues to an avalanche photodiode array, and the data is processed to generate an absorption spectrum of the excited state. Since all the molecules in the sample will not undergo the same dynamics simultaneously, this experiment must be carried out many times, and the data must be averaged in order to generate spectra with accurate intensities and peaks. Ultrafast transient absorption can use almost any probe light, so long as the probe is of a pertinent wavelength or set of wavelengths. A monochromator and photomultiplier tube in place of the avalanche photodiode array, allows observation of a single probe wavelength, and thus allows probing of the decay kinetics of the excited species. The purpose of this setup is to take kinetic measurements of species that are otherwise nonradiative, and specifically it is useful for observing species that have short-lived and non-phosphorescent populations within the triplet manifold as part of their decay path. It should be noted that the pulsed laser in this setup is used both as a primary excitation source, and a clock signal for the ultrafast measurements. Although laborious and time-consuming, the monochromator position may also be shifted to allow absorbance decay profiles to be constructed, ultimately to the same effect as the above method. Time-resolved photoelectron spectroscopy and two-photon photoelectron spectroscopy[ edit ] Time-resolved photo-electron spectroscopy and two-photon photoelectron spectroscopy 2PPE combine a pump-probe scheme with angle-resolved photoemission. A first laser pulse is used to excite a material, a second laser pulse ionizes the system. The kinetic energy of the electrons from this process are then detected, through various methods including energy mapping, time of flight measurements etc. As above, the process is repeated many times, with different time delays between the probe pulse and the pump pulse. This builds up a picture of how the molecule relaxes over time. A variation of this method looks at the positive ions created in this process, and is called time-resolved photo-ion spectroscopy TRPIS Multidimensional spectroscopy[ edit ] Using the same principles pioneered by 2D-NMR experiments, multidimensional optical spectroscopy is possible using ultrafast pulses. Different frequencies can probe various dynamic molecular processes to differentiate between inhomogeneous and homogeneous line broadening as well as identify coupling between the measured spectroscopic transitions. If two oscillators are coupled together, be it intramolecular vibrations or intermolecular electronic coupling, the added dimensionality will resolve anharmonic responses not identifiable in linear spectra. A typical 2D pulse sequence consists of an initial pulse to pump the system into coherent superposition of states, followed by a phase conjugate second pulse that pushes the system into a non-oscillating excited state, and finally, a third pulse that converts back to a coherent state that produces a measurable pulse. Multidimensional spectroscopy exist in infrared and visible variants as well as combinations using different wavelength regions. Ultrafast imaging[ edit ] Most ultrafast imaging techniques are variations on standard pump-probe experiments. Some commonly used techniques are Electron Diffraction imaging, [6] Kerr Gated Microscopy, [7] imaging with ultrafast electron pulses [8] and terahertz imaging. This is particularly true in the biomedical community where safe and non-invasive techniques for diagnosis are always of interest. Terahertz imaging has recently been used to identify areas of decay in tooth enamel and image the layers of the skin. Additionally it has shown to be able to successfully distinguish a region of breast carcinoma from healthy tissue. Femtosecond up-conversion[ edit ] Femtosecond up-conversion is a pump-probe technique that uses nonlinear optics to combine the fluorescence signal and probe signal to create a signal with a new frequency via photon upconversion , which is subsequently detected. The probe scans through delay times after the pump excites the sample, generating a plot of intensity over time. Until the advent of femtosecond methods, many of the

mechanism of such processes were unknown. Photodissociation and femtosecond probing[ edit ] Photodissociation is a chemical reaction in which a chemical compound is broken down by photons. It is defined as the interaction of one or more photons with one target molecule. Any photon with sufficient energy can affect the chemical bonds of a chemical compound, such as visible light, ultraviolet light, x-rays and gamma rays. The technique of probing chemical reactions has been successfully applied to unimolecular dissociations. The possibility of using a femtosecond technique to study bimolecular reactions at the individual collision level is complicated by the difficulties of spatial and temporal synchronization. One way to overcome this problem is through the use of Van der Waals complexes of weakly bound molecular cluster. Femtosecond techniques are not limited to the observation of the chemical reactions, but can even be exploited to influence the course of the reaction. This can open new relaxation channels or increase the yield of certain reaction products.

## 3: Laser Spectroscopy: Basic Concepts and Instrumentation - Wolfgang Demtröder - Google Books

*Linear methods of laser spectroscopy are based on elementary processes of interaction of one photon with the molecular system. Let the photon has the energy  $h\nu$  ( $\nu$  is the photon frequency), and  $B(j)$  is the heavy particle in the quantum state  $j$ .*

The red bands indicate "dirty" particles while cleaner ice particles are shown as turquoise in the outer parts of the rings. Raman, Raman spectroscopy measures the scattering of monochromatic light caused by a sample. The beam from an argon-ion laser is directed by a system of mirrors to a lens, which focuses monochromatic light onto the sample. Most of the light bouncing off the sample scatters at the same wavelength as the incoming light, but some of the light does scatter at different wavelengths. This happens because the laser light interacts with phonons, or naturally occurring vibrations present in the molecules of most solid and liquid samples. These vibrations cause the photons of the laser beam to gain or lose energy. The shift in energy gives information about the phonon modes in the system and ultimately about the molecules present in the sample. Fluorescence refers to the visible radiation emitted by certain substances because of incident radiation at a shorter wavelength. In laser-induced fluorescence LIF, a chemist activates a sample usually with a nitrogen laser alone or a nitrogen laser in combination with a dye laser. This excitation lasts for a few nanoseconds before the electrons return to their ground state. As they lose energy, the electrons emit light, or fluoresce, at a wavelength longer than the laser wavelength. Because the energy states are unique for each atom and molecule, the fluorescence emissions are discrete and can be used for identification. For instance, some countries have adopted LIF to protect consumers from pesticide-tainted vegetables. The tool itself consists of a nitrogen laser, a sensor head and a spectrometer, all packaged in a small, portable system. In some cases, the pesticides can be identified directly. In other cases, they must be identified based on how they interact with chlorophyll, the green pigment present in all leaves. The "P" in ICP stands for plasma, an ionized gas consisting of positive ions and free electrons. In nature, plasmas usually form only in stars, where the temperatures are high enough to ionize the gas. But scientists can create plasmas in the lab using something known as a plasma torch. The torch consists of three concentric tubes of silica surrounded by a metal coil. When an electric current passes through the coil, a magnetic field is created, which in turn induces electric currents in a gas, usually argon, allowed to pass through the silica tubes. This excites the argon gas and creates the plasma. A nozzle at the end of the torch acts as an exit for the plasma. Now the instrument is ready to analyze a sample.

## 4: Spectroscopy | science | www.enganchecubano.com

*Introduction to Laser Spectroscopy is a well-written, easy-to-read guide to understanding the fundamentals of lasers, experimental methods of modern laser spectroscopy and applications. It provides a solid grounding in the fundamentals of many aspects of laser physics, nonlinear optics, and molecular spectroscopy.*

YAG solid-state laser and a spectrometer with a wide spectral range and a high sensitivity, fast response rate, time gated detector. This is coupled to a computer which can rapidly process and interpret the acquired data. As such LIBS is one of the most experimentally simple spectroscopic analytical techniques, making it one of the cheapest to purchase and to operate. YAG laser generates energy in the near infrared region of the electromagnetic spectrum, with a wavelength of nm. Other lasers have been used for LIBS, mainly the Excimer Excited dimer type that generates energy in the visible and ultraviolet regions. The spectrometer consists of either a monochromator scanning or a polychromator non-scanning and a photomultiplier or CCD detector respectively. The most common monochromator is the Czerny-Turner type whilst the most common polychromator is the Echelle type. However, even the Czerny-Turner type can be and is often used to disperse the radiation onto a CCD effectively making it a polychromator. The polychromator spectrometer is the type most commonly used in LIBS as it allows simultaneous acquisition of the entire wavelength range of interest. The spectrometer collects electromagnetic radiation over the widest wavelength range possible, maximising the number of emission lines detected for each particular element. All elements have emission lines within this wavelength range. The energy resolution of the spectrometer can also affect the quality of the LIBS measurement, since high resolution systems can separate spectral emission lines in close juxtaposition, reducing interference and increasing selectivity. This feature is particularly important in specimens which have a complex matrix, containing a large number of different elements. Advantages[ edit ] Because such a small amount of material is consumed during the LIBS process the technique is considered essentially non-destructive or minimally-destructive, and with an average power density of less than one watt radiated onto the specimen there is almost no specimen heating surrounding the ablation site. Due to the nature of this technique sample preparation is typically minimised to homogenisation or is often unnecessary where heterogeneity is to be investigated or where a specimen is known to be sufficiently homogeneous, this reduces the possibility of contamination during chemical preparation steps. One of the major advantages of the LIBS technique is its ability to depth profile a specimen by repeatedly discharging the laser in the same position, effectively going deeper into the specimen with each shot. This can also be applied to the removal of surface contamination, where the laser is discharged a number of times prior to the analysing shot. LIBS is also a very rapid technique giving results within seconds, making it particularly useful for high volume analyses or on-line industrial monitoring. LIBS is an entirely optical technique, therefore it requires only optical access to the specimen. This is of major significance as fiber optics can be employed for remote analyses. And being an optical technique it is non-invasive, non-contact and can even be used as a stand-off analytical technique when coupled to appropriate telescopic apparatus. These attributes have significance for use in areas from hazardous environments to space exploration. Additionally LIBS systems can easily be coupled to an optical microscope for micro-sampling adding a new dimension of analytical flexibility. This is very significant as chemical imaging is becoming more important in all branches of science and technology. Portable LIBS systems are more sensitive, faster and can detect a wider range of elements particularly the light elements than competing techniques such as portable x-ray fluorescence. And LIBS does not use ionizing radiation to excite the sample, which is both penetrating and potentially carcinogenic. Disadvantages[ edit ] LIBS, like all other analytical techniques is not without limitations. It is subject to variation in the laser spark and resultant plasma which often limits reproducibility. The detection limits for LIBS vary from one element to the next depending on the specimen type and the experimental apparatus used. Designed for material analysis, the spectrometer allowed the LIBS system to be sensitive to chemical elements in low concentration. Man-portable LIBS device s developments[ edit ] In the s, interest developed in LIBS that focused on the miniaturization of the components and the development of compact, low-power, portable systems. Recent developments in LIBS

have seen the introduction of double-pulsed laser systems. In perpendicular configuration the laser fires twice on the same spot on the specimen with a pulse separation in the order of one to a couple of tens of microseconds. Depending on pulse separation, the second pulse is more or less absorbed by the plasma plume caused by the previous pulse, resulting in a reheating of the laser plasma leading to signal enhancement. In orthogonal configuration a laser pulse is fired parallel to the sample surface either before or after the perpendicular pulse hits the specimen. The laser plasma ignited in the surrounding medium above the surface by a first pulse causes by its shock wave an area of reduced pressure above the specimen into which the actual plasma from the sample can expand. This has similar positive effects on sensitivity like LIBS performed at reduced pressures. If the orthogonal laser pulse is delayed with respect to the perpendicular one, the effects are similar as in the perpendicular configuration. Timing electronics such as digital delay generators can precisely control the timing of both pulses. It also significantly reduces the matrix effects. Double-pulsed systems have proven useful in conducting analysis in liquids, as the initial laser pulse forms a cavity bubble in which the second pulse acts on the evaporated material. LIBS is one of several analytical techniques that can be deployed in the field as opposed to pure laboratory techniques. As of [update], recent research on LIBS focuses on compact and man-portable systems. Some industrial applications of LIBS include the detection of material mix-ups, [11] analysis of inclusions in steel, analysis of slags in secondary metallurgy, [12] analysis of combustion processes, [13] and high-speed identification of scrap pieces for material-specific recycling tasks. Armed with data analysis techniques, this technique is being extended to pharmaceutical samples. If the pulse duration is long, the newly ionized electrons can be accelerated and eventually avalanche or cascade ionization follows. Once the density of the electrons reaches a critical value, breakdown occurs and high density plasma is created which has no memory of the laser pulse. So, the criterion for the shortness of a pulse in dense media is as follows: A pulse interacting with a dense matter is considered to be short if during the interaction the threshold for the avalanche ionization is not reached. At the first glance this definition may appear to be too limiting. Fortunately, due to the delicately balanced behavior of the pulses in dense media, the threshold cannot be reached easily. A potentially important development to LIBS involves the use of a short laser pulse as a spectroscopic source. The self-luminous plasma is far superior in terms of low level of continuum and also smaller line broadening.

## 5: Ultrafast laser spectroscopy - Wikipedia

*"Proceedings of the Fritz Haber International Symposium on Methods of Laser Spectroscopy, held December , , at the Weizmann Institute of Science Rehovot, Israel and Ein-Bokek, Dead Sea, Israel"--Title page verso.*

You are not yet listed? Usually, the strength of some interaction is measured as a function of the wavelength or optical frequency ; i. There exists a very wide range of very different spectroscopic methods; this article can give only a course overview. Many of the modern spectroscopic methods involve one or several lasers and are then called laser spectroscopy. Due to the enormous potentials of lasers in terms of temporal and spatial coherence , narrow linewidth and wavelength tunability , optical power particularly peak power , ultrashort pulse generation etc. Even before that time, spectroscopy has delivered invaluable insight into many phenomena; for example, it allowed researchers to study the interior of the sun and discover helium there, even before it was found on earth. Exploited Physical Effects Absorption of Light Different interactions between light and matter can be utilized in spectroscopy. For example, atoms and molecules exhibit distinct absorption features, so that different atoms or molecules can easily be distinguished if the absorption versus wavelength is measured. Particularly in the mid- infrared spectral region, molecules have relatively strong and narrow absorption lines related to their vibrational and rotational modes. This allows one to detect a wide range of substances with a very high sensitivity. An example for an application is the detection of tiny concentrations of air pollutants. As molecules can have many different absorption lines, some of which may overlap for different species, detection of a single line is often not sufficient for discriminating between different molecules. Recording the absorption spectrum for some sufficiently wide wavelength range, however, often results in a clear spectroscopic finger print. One may also distinguish different isotopes. The mid-infrared spectral region is quite ideal for sensitive spectroscopy e. For example, one may apply difference frequency generation in nonlinear crystal materials , requiring two input wavelengths and often leading to quite low optical powers. Other challenges are that it is more difficult to obtain optical materials with high transmission at long wavelengths and also sensitive photodetectors. Therefore, one often exploits overtones, i. However, such overtone absorption bands are weaker and thus often result in a lower sensitivity. A low absorption coefficient can still allow for a high sensitivity if the pass length of light is increased accordingly. Therefore, one uses multipass gas cells , where a long path length can be realized in a still relatively compact cell. There are also resonant techniques, where one uses absorption inside a passive optical resonator e. In the latter case, one may e. Even weak absorption features can lead to pronounced dips in the measured spectrum as that absorption applies in many subsequent resonator round-trips. Spectroscopy is not only applied to microscopic particles, but also to macroscopic objects such as optical resonators. For example, a high- finesse stable optical resonator can be used as an optical frequency standard and probed with spectroscopic methods. Other Effects of Absorption Usually, the measured effect in spectroscopy is the reduction in optical power due to the absorption. However, there are also other possibilities. For example, in photoacoustic spectroscopy one exploits the generation of sound by absorption of light from a power-modulated source. The absorbed light leads to some heating, which causes expansion of the gas and thus generates a sound wave, which can be detected with a sensitive microphone. Emission or Scattering of Light Matter can also be excited to emit or scatter light with characteristic features. This is already possible with simple heating or by illumination with sun light. For example, a spectrometer on a satellite may record spectra of scattered light from the earth surface in order to distinguish rocks, plants, lake surfaces, etc. Many advanced spectroscopic methods use the illumination of a sample with a laser source. The absorbed light may not only lead to heating, but also excite atoms or molecules, which then subsequently emit fluorescence light. An example for such methods is the investigation of laser gain media. A laser beam with suitable optical frequency can excite laser-active ions into metastable states , from which they may be further excited for sufficiently high optical intensities or get back to the ground state, emitting fluorescence light. The fluorescence spectrum is related to the wavelength-dependent emission cross sections , which are relevant for the achievable laser gain. One may also detect the decay of fluorescence intensity after excitation with a short laser pulse in order to determine the

upper-state lifetime. With a combination of spectroscopic techniques, one may achieve a comprehensive characterization of the physical details of laser gain media such as laser crystals or rare-earth-doped fibers [8]. One may even study subtle effects such as interactions between different laser-active ions, leading to energy transfer phenomena. The spectrum of Raman-scattered light which is separated from the pump light with a special narrow-band dichroic optical filter such as Rugate filters contains information on molecular vibrations. High-energy Lidar systems, as used e. Here, one may e. A variety of methods has been developed which allow the remote measurement of many properties such as temperature, pressure, trace gas concentrations and cloud particle densities. Phase Changes In some spectroscopic methods, one exploits changes of the optical phase. Typically, an interaction of interest occurs in one arm of an interferometer. The resulting phase changes can be sensitively detected because they are turned into power changes at the interferometer output. Phase changes resulting from absorption lines are also relevant in frequency modulation spectroscopy. Methods of Spectroscopy Spectral Decomposition of Transmitted Light One may use a broadband light source white light source and then apply a spectral decomposition in the photodetection system. Often, a high spectral sensitivity is obtained by combining the photodetector with some kind of monochromator. A high-resolution spectrometer, for example, allows measurements for many different narrow wavelength bins without precisely controlling a light source. The measurement time may be long if each wavelength is treated separated and there are many narrow wavelength bins, but some spectrometers can simultaneously record many wavelengths, e. A special way of obtaining spectral resolution is the use of an interferometer where an arm length is scanned during the measurement. With a narrow-band light source, that would result in a simple sinusoidal oscillation of the output power. With a broadband source, however, one obtains a superposition of many different oscillations. Using a Fourier transform, one can retrieve the spectrum. Interferometric wavemeters have a similar working principle. Such methods are called Fourier transform spectroscopy. Many modern infrared spectrometers are based on such techniques. Variation of the Source Wavelength In many cases, spectroscopy is done with a wavelength-tunable light source. Various such sources are discussed below. One may then, for example, measure the absorption of a sample as a function of the emission wavelength of the laser. As it is more difficult to make a widely tunable narrow-band laser source, that technique often leads to a smaller tuning range  $\Delta\lambda$  smaller than the range possible with a simple broadband light source. However, the method offers superior resolution and also rapid data acquisition with low noise, as one can obtain a relatively strong detector signal. Note that all available optical power is concentrated on a particular wavelength of interest, rather than spread over the whole measurement range. As the optical power often somewhat varies with wavelength and possibly also with time, a high precision requires monitoring of that power. This can be done, for example, in two-beam spectrometers, where the light from the source is split into two beams. Only one beam the sample beam, but not the reference beam, is sent through the medium under investigation, and the powers or intensities of both beams are measured. Particularly high sensitivities can be obtained with balanced photodetectors, where one directly measures the difference of photocurrents from the two beams. Exploitation of Nonlinear Effects When high-intensity light sources normally lasers are used, one may exploit various nonlinear optical effects for spectroscopy. Raman spectroscopy has already been mentioned above. Two-photon absorption has been utilized for a long time [6]. Another important example is coherent anti-Stokes Raman spectroscopy CARS, where two input waves generate a detected signal with slightly higher optical frequency via four-wave mixing. Various other nonlinear effects, such as Brillouin scattering, can be exploited with other methods. Elimination of Doppler Effects Atoms and molecules in gases can exhibit substantial Doppler broadening of their absorption lines due to their thermal motion. There are, however, various methods of Doppler-free spectroscopy. For example, this can involve counterpropagating laser beams, where a probe beam in one direction selects a certain velocity class via absorption saturation [1], and the other beam detects that saturation. This method is called Doppler-free saturation spectroscopy [26]. Terahertz Spectroscopy A relatively new field is terahertz spectroscopy [21], where terahertz radiation with frequencies  $\nu$ . Although lasers cannot directly emit terahertz radiation, they can be used in different waves for generating such radiation, e. Also, ultrashort pulse lasers are useful for the time-resolved detection of terahertz waves. As many optically opaque materials have a substantial

transparency for terahertz radiation, terahertz spectroscopy can be used for a wide range of investigations in science and technology. For example, it is now used for fault location in airplane parts and in security screenings. Frequency Combs Some techniques of modern laser spectroscopy employ frequency combs as generated with mode-locked lasers [15]. As such a frequency comb contains some number of exactly equidistant lines in the spectrum, all of its frequency components are known apart from some noise if only two parameters are fixed possibly stabilized with some feedback techniques: Therefore, frequency combs can serve for extremely precise frequency measurements in wide wavelength ranges, if they are produced with a high optical bandwidth sometimes more than octave-spanning and with proper frequency stabilization. There are various important applications in frequency metrology in particular, ultraprecise optical clocks and other fields. High Temporal Resolution Spectroscopy may also involve measurements with an extremely high temporal resolution. In pump-probe spectroscopy one uses an ultrashort pump pulse, followed by a probe pulse with a variable time delay between a few femtoseconds and several nanoseconds. The effect of the pump pulse on the sample and thus on the probe pulse can be measured as a function of the time delay, which is often adjusted simply via a variable optical path length. An alternative is to use two mode-locked lasers with slightly different pulse repetition rates, so that a range of time delays is scanned continuously. Lasers for Spectroscopy Due to the enormously wide range of methods for laser spectroscopy, there is also a wide range of different laser sources which are used for such purposes: Small single-frequency laser diodes can be used as cheap and compact wavelength-tunable sources. The emission wavelength is often tuned simply by varying the drive current, which affects the temperature. More refined schemes involve an external laser resonator containing wavelength-selective optical elements. Such external cavity diode lasers allow for higher performance. MgSiO<sub>4</sub> forsterite lasers and erbium-doped fiber lasers can be quite useful for spectroscopy, as they can cover wavelength ranges of tens to hundreds of nanometers and often also provide a substantial output power and low noise. In some cases, Q-switched operation with the generation of nanosecond pulses is useful; important examples are laser-induced breakdown spectroscopy and Lidar.

## 6: Spectroscopy - Wikipedia

*Methods of Laser Spectroscopy - Ebook written by Yehiam Prior, Abraham Ben-Reuven, Michael Rosenbluh. Read this book using Google Play Books app on your PC, android, iOS devices. Download for offline reading, highlight, bookmark or take notes while you read Methods of Laser Spectroscopy.*

Time-integrated laser-induced fluorescence spectroscopy is one of the most sensitive techniques based on the interaction between light and matter. It works on the basis of registering direct radiation emitted by the substances to be detected, and offers exceptional detection sensitivity and spatial resolution. Frequently, the essential requirements for an additional, specific production step cannot be controlled sufficiently, since most laboratory methods provide only limited and randomly appropriate information. Principle of time-integrated fluorescence detection. An efficient inline and online process analysis can, therefore, contribute significantly to the prevention of quality defects. The reduction in production losses saves resources and essentially increases the added value of a process. In principle, the required surface analysis can be divided into two different application areas: Common methods – chemical analysis, thermal treatment of product samples with a subsequent gravimetric evaluation, or CO<sub>2</sub> total organic carbon, or TOC gas analysis – are based on taking product samples. Plasma or mass spectroscopy are vacuum-based methods, where an invasive interaction with the respective surface takes place. Comparatively, optical methods have the big advantage of an analysis without any contact to the surface to be investigated. However, most currently used methods, such as IR-, Raman- or diffuse-reflectance spectroscopy, as well as the ellipsometry, are dependent on constant reflection properties of the examined product surface. Furthermore, to determine a surface amount or layer thickness derived from transmission or absorption behavior, an initial intensity is always needed as a reference value. The special time-integrated laser-induced fluorescence spectroscopy, or LIF, technique is a process-analytic, contact-free procedure that allows a nondestructive analysis of the surface cleanliness directly in production processes. The method can also be applied for qualitative and quantitative monitoring of lubrications or other applied functional coatings. Physical and technical principle The basic principle of laser-induced fluorescence spectroscopy is the absorption of the exciting laser radiation through the substance to be detected. In this process, an interaction of laser radiation with fluorophore regions in the electron structures of the target molecule takes place. This process is one of the most efficient interactions between light and matter, and it occurs in dependency of the substances involved and substrate media, with measurably different speeds. A statistical registration of the single photons here offers, in comparison to other spectroscopic methods, a detection of very low quantities of material with particularly high sensitivity. Laser emission in the UV spectral range. Therefore, a time-integrating approach is included in the procedure to observe the decay times of fluorescence signals in a suitable wavelength range. After each single laser pulse excitation, lasting about 0. Here, the time-integrated intensity is measured as values I<sub>1</sub> and I<sub>2</sub> in order to separate the wanted signal from the background, as indicated in Figure 1. Optical excitation is performed by a specially designed, passively Q-switched UV microchip laser from Teem Photonics SA with a repetition frequency in the range of 11 kHz. Single laser pulses with an emission wavelength of or nm and an average optical output power below 2 mW are generated. These are transferred via a quartz fiber bundle of up to 20 m in length and a probe head directly into the process. With a second quartz fiber bundle, the transmission of fluorescence signals to the detector is arranged. Therefore, the corresponding detection head contains no active components, and is suitable to be used in harsh and demanding environmental conditions. If there is a risk of contamination of the fiber optics, automated pollution prevention is ensured by using a compressed air or gas flushing, or appropriate ultrasound techniques. Figure 2 shows examples of three different configurations for various applications of inline surface analysis. Different configurations of detection heads for surface analysis: By choosing the configuration and positioning of the probe distance and angle with respect to the surface of investigation, the spot size of the effective detection area can be adapted to the process requirements. For a very sensitive detection of single-fluorescence light events photons, a photomultiplier tube is used. An application-specific wavelength configuration is provided by a special combination of optical filters in front of

the detector. Using a statistical single-photon counting method, the detector pulses are evaluated according to the time-integrated method. Via a calibration function, the respective measured quantity is calculated and displayed depending on the application with a high sampling rate of every 10 ms or even every second. Figure 3 demonstrates schematically the technical implementation of the time-integrated laser-induced fluorescence analysis. Schematic setup of the time-integrated fluorescence detection system. Industrial applications A versatile field of application of coating analysis is the specific detection of lubricants on coil material single boards, and on prefabricated parts in the steel and aluminum industries. Coil material is customer-specific and lubricated with different kinds of prelubes for the automotive industry. Figure 4a shows a typical installation of a system for simultaneous inspection of the upper and lower surfaces of coil material with a width of up to 2 m. It was integrated in an existing production line. For the measurements, two single detection heads with compressed-air flushing Figure 2c are synchronously moved with a travel speed of 0. Figure 4b demonstrates typical results for the top and bottom surface, each in separate color gradient plots. The green indicates an optimum accordance with the predefined amount of prelube for the lubrication; the blue color indicates an over-oiling. The red is a warning for dry areas, which in most cases are not observable by a direct visual inspection. Fluorescence detection system for a simultaneous inline and online inspection of the top and bottom sides of lubricated coil material: Beyond lubrication control, there is a variety of other applications in the field of metal processing, where the inline monitoring of special functional layers might increase the process efficiency, or lead to better, more stable and reliable product quality. Some examples include passivation coatings, lacquers, films, polymers, primers and adhesives. In the metal working industry, large amounts of production additives, such as cooling lubricants, are used to ensure high process reliability in forming or machining production. Residuals of these coatings remain as contaminants on the workpiece surface and will be unavoidably carried over into subsequent process steps. Special manufacturing processes are very sensitive to the surface cleanliness of the working material, such as annealing, bonding, coating, painting, etc. Therefore, in most applications, the workpiece is cleaned prior to further processing. The continuous monitoring and evaluation of technical surfaces concerning residues of process additives and cleaning media is another important application of the fluorescence spectroscopic surface analysis. Typical results for detection of rolling-oil residues on aluminum sheets: In the case of production that uses the rolling process, aluminum, steel or copper sheets are annealed in order to remove remaining rolling oil on the surface. Figure 5 shows the results of such a determination of rolling-oil residues on aluminum sheets. The results were determined subsequent to the fluorescence measurements with a standard surface carbon analyzer, based on the determination of the TOC.

### 7: USA1 - Modulation cancellation method in laser spectroscopy - Google Patents

*The Fritz Haber Symposium on Methods of Laser Spectroscopy was held in Ein Bokek, Israel, on the shores of the Dead Sea, on December ,*

In practice, making such precise measurements is extremely difficult due to small variations in temperature, pressure, and other external factors. The most common tool for this type of measurements is a mass-spectrometer MS. MS provides the required accuracy, but there are a number of shortcomings associated with this technology. Mass spectrometers are expensive, bulky and in general can not be used in the field. A sample preparation is required that can potentially affect the isotopic composition. Confusion between molecules or molecular fragments with similar masses is possible. Infrared molecular absorption spectroscopy is considered as a viable alternative to MS, but few groups have succeeded in achieving the required accuracy even in laboratory experiments Current optical instrumentation for determination of isotopic composition is based on separate precise measurements of the strength of absorption lines corresponding to two isotopes with the subsequent numerical comparison. Hence, a small difference between isotopic compositions of the analyzed sample and the reference sample is determined as a difference between two large numbers concentration ratios. Some of the issues adding to the error of such an approach are: Another problem with present laser spectroscopic techniques has been the detection of species with broad irresolvable absorption features, which is a characteristic of many polyatomic molecules. In such cases, a semiconductor laser usually can not be wavelength modulated with a swing sufficient to cover the whole absorption feature. Thus, detection of such molecules would require amplitude modulation of the laser radiation. The scattered and subsequently absorbed light creates an incoherent background, making low-level concentration measurements difficult. Accordingly, there is a need for a simple method of accurately measuring small deviations in concentration ratios using laser spectroscopy. It is further desired to provide a laser spectroscopic method to detect minute concentrations of complex molecules. Thus, the disclosed methods and systems significantly increase the sensitivity and accuracy of laser spectroscopic measurements. These and other needs in the art are addressed in one embodiment by a method for measuring a concentration of a first and a second compound in a sample composition. The method comprises providing at least a first and a second modulated light beam having a first and a second wavelength, respectively. The second modulated light beam is phase shifted from the first modulated light beam. The method also comprises passing the first and the second modulated light beam through a reference composition. The reference composition comprises a reference concentration of the first and the second compound. In addition, the method comprises detecting a reference signal resulting from the absorption of the first and second modulated light beam by the reference composition. Moreover, the method comprises adjusting the amplitude of the second modulated light beam such that no reference signal is detected. Additionally, the method comprises passing the first modulated light beam and the second modulated light beam through a sample composition. The method further comprises detecting a sample signal so as to measure the concentration of the first and the second compound in the sample composition. In another embodiment, a method for measuring the concentration of a compound having a background wavelength and an absorption wavelength comprises providing at least a first and a second modulated light beam, wherein the second modulated light beam is phase shifted from the first modulated light beam. The method also comprises tuning the first modulated light beam to the background wavelength of the compound and the second modulated light beam to the absorption wavelength of the compound. Moreover, the method comprises tuning the amplitude of the second modulated light beam such that no signal is detected when the first and the second modulated light beam are passed through a composition lacking the compound. In addition, the method comprises passing the first and the second modulated light beam through a sample composition. The method further comprises detecting a signal indicative of the concentration of the compound in the sample composition. In a further embodiment, a laser spectroscopic system comprises a first and a second light source. The first and said second light source emit a first and second modulated light beam, respectively. The second beam is phase shifted from the first modulated light beam. Furthermore, the system comprises a

sample cell including a sample detector. The sample cell contains a sample composition comprising a first and a second compound. The first and said second modulated light beam pass through the sample cell. The system additionally comprises a reference cell including a reference detector. The reference cell contains a reference concentration of the first and the second compound. The first and said second modulated light beam pass through said reference cell. Moreover, the system comprises an attenuator coupled to said reference detector and said second light source. The attenuator controls the second light source to match the amplitude of the second modulated light beam to the amplitude of the first modulated light beam such that no signal is detected from the reference detector. The foregoing has broadly outlined the features and technical advantages of the present invention in order that the detailed description of the invention that follows may be better understood. Additional features and advantages of the invention will be described hereinafter that form the subject of the claims of the invention. It should be appreciated by those skilled in the art that the conception and the specific embodiments disclosed may be readily utilized as a basis for modifying or designing other structures for carrying out the same purposes of the present invention. It should also be realized by those skilled in the art that such equivalent constructions do not depart from the scope of the invention as set forth in the appended claims. First and second light source, typically each comprise a tunable laser device. However, first and second light source, may comprise any suitable light emitting device. In certain embodiments, first and second light source, comprise distributed-feedback diode lasers. Alternatively, first and second light source, are quantum cascade lasers. First light source generates a first modulated light beam and second light source generates a second modulated light beam. As defined herein, a modulated light beam is a beam of radiation in which the wavelength or amplitude of the beam of radiation is varied or modulated at a particular modulation frequency. In further embodiments, laser spectroscopic system includes a first and second beam splitter, First and second beam splitter, split first and second beams, and direct each respective beam to first and second polarization controllers, and first and second calibration cells, respectively. First and second cells, typically each comprise a photodetector such as a photodiode, although other types of photodetectors may be utilized. In general, each cell, contains a reference concentration of a compound. Specifically, first cell contains a reference concentration of a first compound while second cell contains a reference concentration of a second compound. The photodetector from each cell is coupled to a controller which in turn is coupled to first and second current controllers, First and second current controllers, adjust the wavelength of first and second light sources, According to another embodiment, system also includes a controller such as a low-power digital signal microprocessor. However, any suitable microprocessors may be used with the laser spectroscopic system. Other examples of suitable processors include without limitation, field programmable gate arrays, microcontrollers, programmable logic devices, application specific integrated circuits and the like. As shown in FIG. In other embodiments, additional controllers not shown may be coupled to first and second lock-in amplifiers and first and second light source, The additional controllers may be used to calibrate or tune the modulation frequency of first and second modulated light beams, in embodiments utilizing resonant acoustic detectors. In embodiments, controller includes memory. Memory may comprise volatile e. In a preferred embodiment, memory is flash memory. Memory may be used to store data or code e. The executable code may be executed directly from the non-volatile memory or copied to the volatile memory for execution therefrom. Laser spectroscopic system may also include memory external to controller. This external memory is generally coupled to controller and may comprise either volatile or non-volatile memory. In general, first and second compound may be any material or chemical. Additionally, the first and second compound may be a gas or a liquid. In preferred embodiments, the second compound is an isotope of the first compound. By way of example only, the first compound may comprise H<sub>2</sub> 16O while the second compound may comprise H<sub>2</sub> 18O. Other examples of the first and second compounds include without limitation, 12C- and 13C-containing species, 32S- and 34S-containing species, 14N and 15N containing species, or H- and D-containing species. In one embodiment, the system includes a polarization combiner-splitter which combines first and second beam, into a combined beam not shown and splits it into a first and second combined beam, as seen in FIG. However, the first and second modulated light beams, may be combined by any suitable means including, without limitation, a wavelength division multiplexer, a polarization combiner, or diffraction grating. In

addition, the system may incorporate a separate beam combiner and beam splitter to combine first and second beam, and split the combined beam. In at least one embodiment, the system comprises an attenuator. Attenuator may be any device known to one of ordinary skill in the art used to adjust the intensity of a light beam. Depending on the embodiment, attenuator may be used to adjust first or second beam. In the embodiment shown in FIG. As will be described in more detail below, attenuator may utilize signals from reference detector via second lock-in amplifier to adjust intensity of second beam. In an embodiment, system comprises a sample cell and a reference cell. Sample and reference cells, generally comprise sample and reference detectors, which serve to detect signals from sample and reference cells, respectively. In any case, first and second cells, generate sample and reference output signals, respectively. Moreover, sample and reference cell, contain the sample and reference compositions, respectively. The sample composition generally comprises a concentration of the first and the second compound while the reference composition comprises a known or reference concentration ratio of the first and second compound. As will be described in further detail below, the described apparatus is used to determine whether the sample composition contains a concentration ratio of the compounds different than the reference composition. According to one embodiment, sample and reference detectors, are used to detect the absorption of the combined beams, by the sample composition and the reference composition. More specifically, the detector in sample cell detects a signal generated because of the absorption of the first and second modulated light beam in combined beam by the sample composition. In a particular embodiment, detector is an acoustic detector such as a microphone, a quartz tuning fork, etc. In other embodiments, detector is a photodetector such as a photodiode. However, detector may be any suitable detector capable of detecting absorption of light by a compound. Similarly, reference detector may comprise a photodetector, an acoustic detector, or any other suitable detector. Sample detector may be coupled to a first lock-in amplifier. Likewise, reference detector may be coupled to a second lock-in amplifier. First lock-in amplifier is generally coupled to an output device or a microprocessor to process the data generated from sample cell not shown. On other hand, second lock-in amplifier is typically coupled to an attenuator as shown in FIG. Attenuator is preferably used to adjust the amplitude of second modulated light beam in response to a signal received from second lock-in amplifier.

## 8: Overview of Laser Spectroscopy | HowStuffWorks

*Keeping abreast of the latest techniques and applications, this new edition of the standard reference and graduate text on laser spectroscopy has been completely revised and expanded.*

See Article History Alternative Title: More recently, the definition has been expanded to include the study of the interactions between particles such as electrons, protons, and ions, as well as their interaction with other particles as a function of their collision energy. Spectroscopic analysis has been crucial in the development of the most fundamental theories in physics, including quantum mechanics, the special and general theories of relativity, and quantum electrodynamics. Spectroscopy, as applied to high-energy collisions, has been a key tool in developing scientific understanding not only of the electromagnetic force but also of the strong and weak nuclear forces. Spectroscopic techniques have been applied in virtually all technical fields of science and technology. Radio-frequency spectroscopy of nuclei in a magnetic field has been employed in a medical technique called magnetic resonance imaging MRI to visualize the internal soft tissue of the body with unprecedented resolution. Microwave spectroscopy was used to discover the so-called three-degree blackbody radiation, the remnant of the big bang. The internal structure of the proton and neutron and the state of the early universe up to the first thousandth of a second of its existence are being unraveled with spectroscopic techniques using high-energy particle accelerators. The constituents of distant stars, intergalactic molecules, and even the primordial abundance of the elements before the formation of the first stars can be determined by optical, radio, and X-ray spectroscopy. Optical spectroscopy is used routinely to identify the chemical composition of matter and to determine its physical structure. Spectroscopic techniques are extremely sensitive. Single atoms and even different isotopes of the same atom can be detected among or more atoms of a different species. Isotopes are all atoms of an element that have unequal mass but the same atomic number. Isotopes of the same element are virtually identical chemically. Trace amounts of pollutants or contaminants are often detected most effectively by spectroscopic techniques. Certain types of microwave, optical, and gamma-ray spectroscopy are capable of measuring infinitesimal frequency shifts in narrow spectroscopic lines. Frequency shifts as small as one part in of the frequency being measured can be observed with ultrahigh resolution laser techniques. Because of this sensitivity, the most accurate physical measurements have been frequency measurements. The table summarizes the electromagnetic spectrum over a frequency range of 16 orders of magnitude. Spectroscopic techniques are not confined to electromagnetic radiation, however. In instances where the probe particle is not a photon, spectroscopy refers to the measurement of how the particle interacts with the test particle or material as a function of the energy of the probe particle.

## 9: Laser-Based Spectroscopy

*Spectroscopy / s p ě k ě tr ě s k ě tm p i / is the study of the interaction between matter and electromagnetic radiation. Historically, spectroscopy originated through the study of visible light dispersed according to its wavelength, by a prism.*

Particles such as electrons and neutrons have a comparable relationship, the de Broglie relations, between their kinetic energy and their wavelength and frequency and therefore can also excite resonant interactions. Spectra of atoms and molecules often consist of a series of spectral lines, each one representing a resonance between two different quantum states. The explanation of these series, and the spectral patterns associated with them, were one of the experimental enigmas that drove the development and acceptance of quantum mechanics. The hydrogen spectral series in particular was first successfully explained by the Rutherford-Bohr quantum model of the hydrogen atom. In some cases spectral lines are well separated and distinguishable, but spectral lines can also overlap and appear to be a single transition if the density of energy states is high enough. Named series of lines include the principal, sharp, diffuse and fundamental series. The various implementations and techniques can be classified in several ways. Type of radiative energy[ edit ] This section does not cite any sources. Please help improve this section by adding citations to reliable sources. Unsourced material may be challenged and removed. June Learn how and when to remove this template message The types of spectroscopy are distinguished by the type of radiative energy involved in the interaction. In many applications, the spectrum is determined by measuring changes in the intensity or frequency of this energy. The types of radiative energy studied include: Electromagnetic radiation was the first source of energy used for spectroscopic studies. Techniques that employ electromagnetic radiation are typically classified by the wavelength region of the spectrum and include microwave, terahertz, infrared, near-infrared, ultraviolet-visible, x-ray, and gamma spectroscopy. Particles, because of their de Broglie waves, can also be a source of radiative energy. Both electron and neutron spectroscopy are commonly used. For a particle, its kinetic energy determines its wavelength. Acoustic spectroscopy involves radiated pressure waves. Dynamic mechanical analysis can be employed to impart radiating energy, similar to acoustic waves, to solid materials. Nature of the interaction[ edit ] The types of spectroscopy also can be distinguished by the nature of the interaction between the energy and the material. Absorption occurs when energy from the radiative source is absorbed by the material. Absorption is often determined by measuring the fraction of energy transmitted through the material, with absorption decreasing the transmitted portion. Emission indicates that radiative energy is released by the material. This feature can be measured in the infrared by instruments such as the atmospheric emitted radiance interferometer. Elastic scattering and reflection spectroscopy determine how incident radiation is reflected or scattered by a material. Crystallography employs the scattering of high energy radiation, such as x-rays and electrons, to examine the arrangement of atoms in proteins and solid crystals. Impedance is the ability of a medium to impede or slow the transmittance of energy. For optical applications, this is characterized by the index of refraction. Inelastic scattering phenomena involve an exchange of energy between the radiation and the matter that shifts the wavelength of the scattered radiation. These include Raman and Compton scattering. Coherent or resonance spectroscopy are techniques where the radiative energy couples two quantum states of the material in a coherent interaction that is sustained by the radiating field. The coherence can be disrupted by other interactions, such as particle collisions and energy transfer, and so often require high intensity radiation to be sustained. Nuclear magnetic resonance NMR spectroscopy is a widely used resonance method, and ultrafast laser spectroscopy is also possible in the infrared and visible spectral regions. Type of material[ edit ] This section does not cite any sources.

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