

INTRODUCTION TO OPTICAL METHODS FOR MEASUREMENT OF NATURAL GAS

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ABSTARCT

Optical spectroscopy methods are finding increased applications in the analysis of natural gas from processing to the point of use. These applications are expected to grow in the coming years.

This paper is aimed at helping beginning-level technicians get a broad overview of this topic. It will cover the fundamentals of optical spectroscopy as applied to natural gas analysis, without the use of rigorous mathematical and physical concepts. The discussion is then followed by each type of spectroscopy that is finding applications in natural gas, including absorption spectroscopy, Raman spectroscopy, and fluorescence quenching spectroscopy. The focus is on field-deployable methods and not laboratory-based techniques.

The instrumentation for each method is also reviewed as well as the advantages and disadvantages of each method as it relates to natural gas analysis. We will also discuss the various methods, current applications, as well as upcoming applications.

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I- INTRODUCTION

Optical spectroscopy is an established group of techniques. These methods all share a fundamental common feature; they use the interaction of electromagnetic waves (e.g. light) with materials to deduce information about the make-up of the material under analysis.

Optical spectroscopy has been around for almost 100 years. Despite this relatively long history, practical industrial applications in the industry have been somewhat of a more recent trend. Field applications (outside of laboratories) have been an even more recent phenomenon.

In the last 20 years, advances in optical components, computing power, and display technologies have worked hand in hand to enable many new applications of field-deployed spectroscopy in many different industries. Wide-ranging applications in medical, semiconductor, environmental, materials, pharmaceutical, food, and energy industries have emerged, making significant contributions to safety and efficiency in these industries.

Applications in natural gas analysis have been one of the more recent areas of development. However, these applications are rapidly growing in both breadth and depth of analytical power applied to natural gas analysis.

Optical spectroscopy enjoys a fundamental advantage over most other methods. This advantage can be summarized in the non-invasive nature of optical spectroscopy. Using photons to determine the quality of materials (including gas) is, in almost all cases, non-invasive. Furthermore, since the “sensor” is not in direct contact with the analyte, it will not undergo a change or “drift”. Therefore, the calibrations or adjustments become less frequent or non-existent. This is a tremendous advantage in the energy sector, where analyzers are installed in remote places and cannot be monitored or “adjusted” on a day-to-day basis.

II- BACKGROUND THEORY

“Light” is a form of electromagnetic (EM) radiation. The full discussion of the nature of EM radiation is beyond the scope of this discussion. However, for our purposes, EM radiation can be thought of as an oscillating electrical field. It is the interaction of this oscillating electrical field and matter that enables optical spectroscopy.

EM waves are typically characterized by their wavelength, i.e. the length of one period in the wave. Figure (A) shows the full spectrum of the electromagnetic spectrum. Gamma rays, which have the shortest wavelength ($\sim 10^{-14}$ m), are the most energetic form of EM radiation. Short Waves (SW), with a wavelength of 100 meters, are typically considered the least energetic form of EM radiation and have been used in radio communications for a very long time.

The region of interest to us is the region from Ultraviolet (wavelength of ~ 200 nm or 2×10^{-7} m) to Mid-Infrared (wavelength of $10 \mu\text{m}$ or 1×10^{-5} m). Shorter wavelengths, such as X-rays and Gamma rays, are usually too energetic to be used for materials identification, although X-rays are used in some analysis techniques.

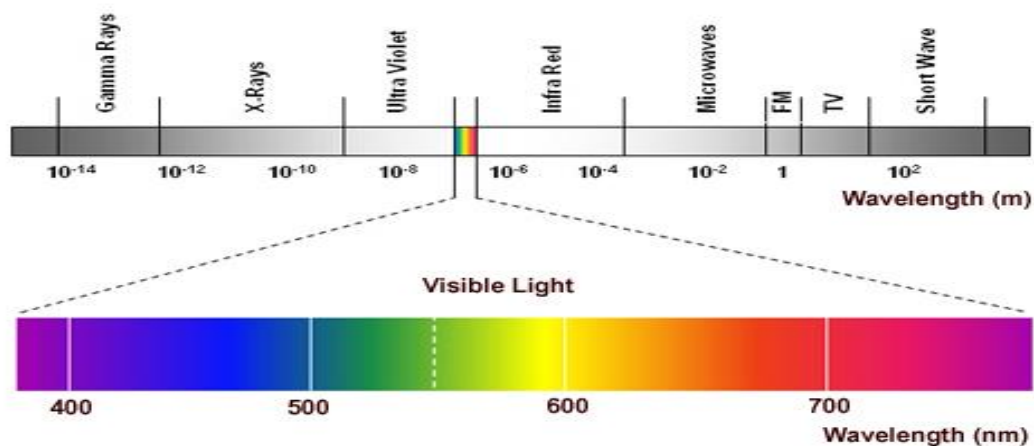


Figure (A)- The Electromagnetic Spectrum

INTERACTION OF EM WAVES AND MATTER

EM waves, whatever their wavelength may be, interact with atoms and molecules. This interaction is the interaction of the oscillating electrical field with the electronic structure of atoms and molecules. By looking at what happens to the light after this interaction, one can deduce information about the molecules in the pathway of the light (gas under analysis). In some cases, temporary changes are induced in the analyte so that it emits new radiation of its own. The makeup of this new emitted “light” will contain clues about the analyte.

III- INSTRUMENTATION COMPONENTS FOR OPTICAL SPECTROSCOPY

Any optical spectroscopy instrument has four components (this is in addition to electronics, power supplies, displays, etc)

1- RADIATION SOURCE

This refers to the source of the optical energy. There are two general categories of sources: a) Lasers and b) Broadband sources.

Lasers, in general, have a spectrally pure output. This means that their output is concentrated in a very narrow wavelength spectrum. Lasers are used as sources in Tunable Absorption Laser Spectroscopy and in Raman Spectroscopy.

Figure (B) shows the output of a common He/Ne laser. Notice that almost all of the intensity of the light is concentrated at 632nm (0.632 μm).

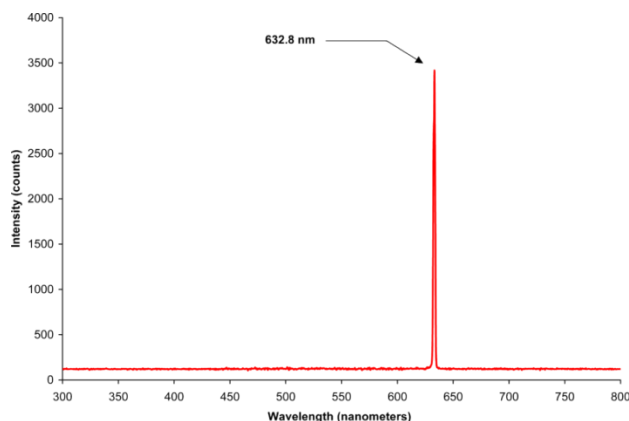


Figure (B)- Output Spectrum of a He/Ne Laser

Broadband sources have a much wider output in terms of wavelength. Most of them are based on a heated element (such as Tungsten filament) and have an output spectrum typical of blackbody radiation. Typical blackbody radiation spectrum is shown in Figure (C). Notice the very broad (spectrally) output profile.

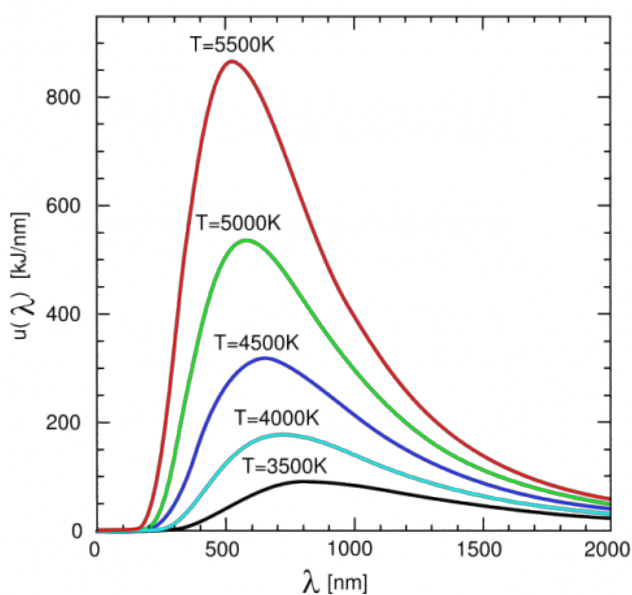


Figure (C) - Blackbody Radiation Spectrum

More recently, diodes have been used in some spectroscopy applications. Diodes typically have spectral output wider than a laser but much narrower than a heated filament.

2- GAS CELL

The gas cell is where the light interacts with the gas under analysis. There may be mirrors in the gas cell to increase the path length of the light within the gas cell.

3- WAVELENGTH SEPARATION/DISCRIMINATION

In order to look at the spectral features, one needs to separate the light into its various wavelengths. This can be done by use of several filters, a tunable filter, a grating, or some other element.

4- DETECTOR(S)

There must be an optical detector, or a detector array, or a set of detectors to measure the various wavelengths. The choice of detector depends on the wavelength of analysis. Detectors are readily available for almost all wavelengths, although they use different technologies in the different wavelength. In the area of up to $2.5\mu\text{m}$, very robust detectors are available.

IV- DIFFERENT TYPES OF OPTICAL SPECTROSCOPY

There are many different variants of optical spectroscopy. For the purposes of this discussion, we will limit ourselves to the methods that have found, or have potential to find applications in natural gas analysis.

ABSORPTION SPECTROSCOPY

Absorption Spectroscopy is a method that has found wide spread application across a range of different industries. From food production and analysis, to pharmaceutical, to environmental, and gas analysis, absorption spectroscopy provides a robust method to discern critical information about products and processes that enable modern industry.

Absorption spectroscopy works on the principle that molecules have different electronic, vibrational, and rotational “states”. When EM waves interact with molecules, molecules will absorb some wavelengths of light, making a transition to a higher “state”. By measuring the amount of absorption in the various wavelengths, one can obtain information about what was in the sample.

Figure (D) below shows a schematic representation of absorption spectroscopy.

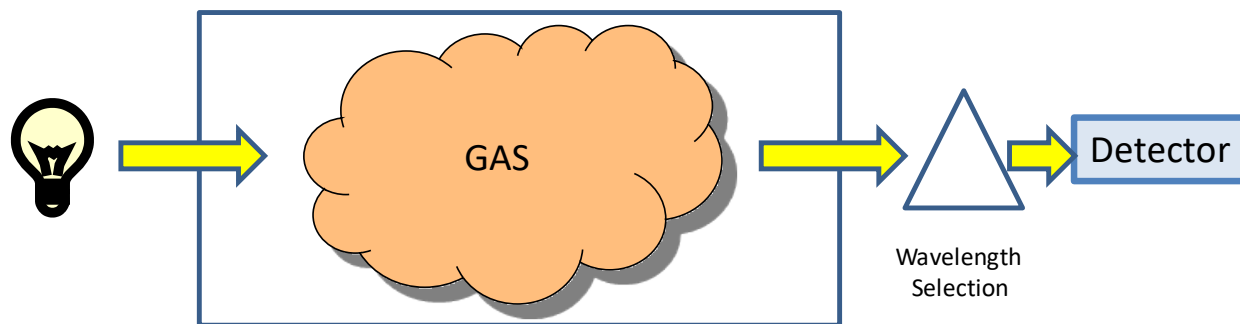


Figure (D)- Schematic of Absorption Spectroscopy

Absorption spectroscopy in the UV and visible regions refers to a situation where the light source is Ultraviolet (200-400nm wavelengths) or Visible (400-700nm wavelengths). These wavelengths, because of their relatively (compared to InfraRed) higher energy, will interact with the electronic states of the molecules. These features are typically broader, and not very

unique and specific for different molecules. Therefore UV and visible absorption spectroscopy have limited applications in natural gas analysis.

The vast majority of absorption spectroscopy applications for gas and liquid analysis happen in the Infrared (IR) region, more specifically Near-IR (NIR) or Mid-IR (MIR) regions which span the wavelength regions of 700nm-15,000nm. In these regions, molecules have very specific absorption “finger-prints”. Therefore IR spectroscopy has found many applications, not only in natural gas analysis, but across a wide spectrum of other industries.

In IR absorption spectroscopy, the oscillating electrical field due to the EM wave will interact with permanent electric dipole moment of a molecule, being absorbed. A molecule has a permanent electrical dipole, if the electronic charges in the molecule are not symmetric (or not balanced). Therefore homo-nuclear diatomic molecules such as N₂, O₂ (as well as atomic gases such as Helium, Neon, etc) do not have a vibrational spectral signature. Consequently, IR absorption spectroscopy cannot be used to detect and measure the concentration of these gases. Figure (E) is a schematic representation of the Nitrogen molecule. Notice that it is symmetrical without any permanent electrical dipole (electrical field). Therefore, it does not have a vibrational spectrum.

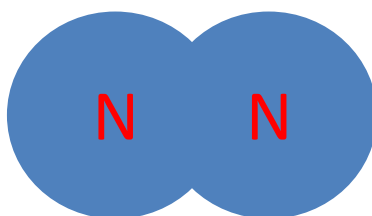


Figure (E) - Nitrogen Molecule (No dipole moment)

A molecule like HF on the other hand, has a permanent electrical dipole moment. The oscillating electrical field in the light will interact with this “charge imbalance”. Figure (F) shows the schematic of the HF molecule with its permanent dipole moment. A portion of the light will get absorbed by the molecule at a specific wavelength corresponding to the “resonant frequency” of this dipole moment. If we monitor the light after it passes through the gas and compare it with the light before its interaction with the gas, we will observe that the intensity of the light at the given wavelength has been reduced by a certain amount which is proportional to the concentration of the gas and the length of the optical path.

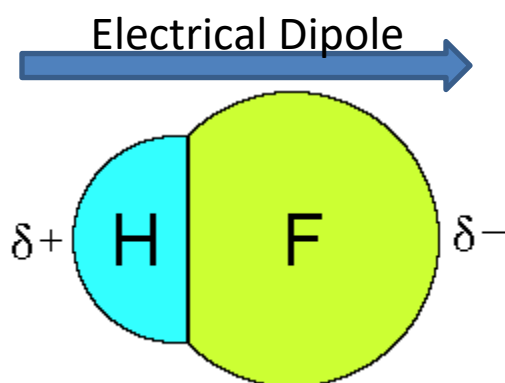


Figure (F)- HF Molecule (permanent dipole moment)

The amount of light absorbed by a gas will depend on several factors. It should be apparent that the “number of molecules” that the light will go through would be one of these factors. The “number of molecules,” in turn, would depend on the concentration of the gas as well as the length of the distance the light would go through the sample. It would also depend on the absorptivity of the specific molecule. Therefore, the absorbance of an analyte can be expressed as:

$$A = \epsilon b c$$

Where A is the absorbance, defined as

$$A = \log_{10} P_0/P$$

P_0 is the original intensity of the light.

P is the intensity of light after going through the sample.

b is the path length of the light.

c is the concentration of the analyte.

ϵ is the molar absorptivity of the analyte.

Conceptually, measuring the concentration of an analyte is simple. The challenge is the instrumentation; picking the right light source, detector, wavelength of analysis, and numerical and electronics signal processing to extract the information.

There are two main types of Infrared absorption spectroscopy used in natural gas analysis. The first type is the conventional type, where the light source is a broadband Infrared source. The second type is Tunable Laser Absorption Spectroscopy (TLAS), where the light source is a tunable laser. We will discuss the TLAS method first.

TUNABLE LASER ABSORPTION SPECTROSCOPY

In TDLAS, a laser is chosen to match a very fine absorption feature of the molecule to be measured. Figure (G) shows a schematic representation of what takes place:

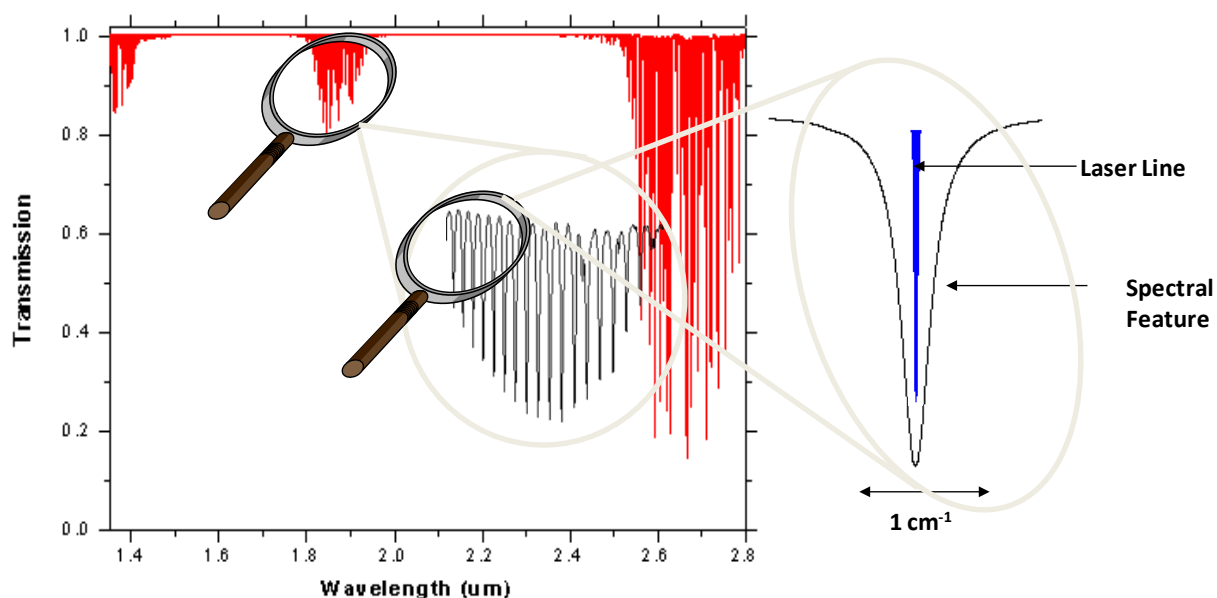


Figure G- Tuning in on an absorption feature

The spectrum shown above is that of water molecule. Water molecule has permanent dipole moment and thus has a strong IR spectral signature as shown above. These features are very narrow in their wavelength profile (at low pressures close to atmospheric pressures). A laser is chosen so that its output wavelength is very close to the wavelength of this spectral feature. Then the laser is tuned back and forth, so that it “scans” this spectral feature. As the laser “come in wavelength focus” (the laser wavelength matches the wavelength of the spectral feature) the molecule will absorb the light strongly. At other times, there is no absorption.

INSTRUMENTATION FOR TUNABLE ABSORPTION SPECTROSCOPY

Recalling from the above section that absorption spectroscopy has four principal components, we can now discuss what these components are for TLAS. The light source is a tunable laser. The wavelength selection device is embedded in the tunable laser. The gas cell is typically a stainless steel tube, which may have mirrors on one or both ends to increase the path length. The detector is a detector that is compatible with the wavelength of the laser source.

One of the variants of TLAS that has found increasing applications is Tunable Diode-Laser Absorption Spectroscopy (TDLAS). In this method, the light source is a tunable diode-laser with an internally built-in grating which enables the laser to output a very narrow line (in terms of wavelength). The laser wavelength is selected such that it matches the absorption wavelength of the gas to be measured.

Diode lasers are available now from UV all the way to around $15\mu\text{m}$. The technology for building them varies at different wavelengths. However, for wavelengths from around 400nm to 2500nm ($0.4\mu\text{m}$ - $2.5\mu\text{m}$), very robust, low-cost lasers are available.

TDLAS enjoys several advantages over other detection methods. The main advantage is selectivity. For a given molecule to be detected, an absorption feature is chosen such that other molecules do not absorb in that spectral region, to give very high selectivity. The laser's power needed is so low that total power consumption is also very low and enabling long-term laser operation.

Another advantage compared to non-optical methods is the non-invasive nature of detection. In normal operation, there should be minimal need for maintenance and calibration.

There are some disadvantages. The most important disadvantage is that TDLAS works best in atmospheric pressure or lower. Therefore, the gas sample cannot be measured at high pressure, typical of gas pipelines. The reason for this limitation is pressure-broadening of absorption features; i.e., the absorption peaks of molecules get wider and merge into each other at higher pressures. Pressure regulation is needed to bring the pressure close to atmospheric pressure, which can cause changes in the gas if not done properly.

The other disadvantage is that liquids in the gas cell can interfere with the measurement. However, this is true of all gas analyzers. In case of TDLAS, using 2f techniques can enhance both sensitivity and improve tolerance to small amounts of liquid.

APPLICATIONS OF ABSORPTION SPECTROSCOPY IN NATURAL GAS ANALYSIS

There are quite a few applications for absorption spectroscopy, and the list is growing. Below, we list some of the more interesting applications in natural gas analysis.

COMPONENT ANALYSIS

Absorption spectroscopy is used to analyze a gas sample and provide a very accurate determination of its components. Given that each molecule occurring in natural gas has a specific “spectral fingerprint”, one can measure the IR spectrum of the gas, and using mathematical techniques (Chemometrics), deduce the concentration of each component.

For this application, typically, a broadband source is used. The wavelength selection device can be a grating or a set of filters, or a tunable filter. The challenge is to design a system that can provide accurate concentration, not only for the dominant components of natural gas (such as methane and light hydrocarbons) but also for the trace components.

DEWPOINT MEASUREMENTS

Traditionally, dewpoints have been “calculated” using GC component analysis and an equation-of-state calculation. However, this method has been shown to have errors over 80°F and is not satisfactory for measurement of dewpoint. This problem has recently been addressed by a variant of IR absorption spectroscopy, called Chilled-Evanescant IR Spectroscopy (CEIRS™)

In this method, an optical crystal is cooled while its surface temperature is being monitored. Simultaneously, IR beams are used to probe the surface of the crystal to detect condensation. As soon as condensation is detected, the temperature is recorded (Dewpoint). By looking at the IR spectrum, one can also determine if the condensate was hydrocarbon or water. Therefore, one can measure both water and hydrocarbon dewpoints with this technique.

This method can work at pressures up to several thousand psi, eliminating pressure regulation errors.

WATER MOISTURE ANALYSIS

Up to recently, the moisture content of gas was mainly measured with electrochemical sensors, which are prone to many different errors, as well as drift in sensitivity and speed of response.

TDLAS has been successfully used to measure trace amounts of water. The challenge here is to design a system that has long optical paths to increase the sensitivity of the unit for the detection of trace amounts. Long optical paths pose mechanical and thermal stability issues that need to be addressed for successful applications.

CEIRS™ technology mentioned above can also be used to measure the dew point of water. Using the dew point and the pressure, one can calculate the water content.

CO2 ANALYSIS

CO₂ has traditionally been measured using IR absorption spectroscopy in many different applications. In natural gas, there are many other molecules that interfere (i.e., have absorption bands that overlap with that of CO₂). Therefore, TDLAS has offered a much more selective technique for measurement of CO₂ in natural gas applications. There are commercial systems that use TDLAS for measurement of CO₂ in natural gas.

H₂S ANALYSIS

Absorption spectroscopy has been used for the detection of sulfur compounds using UV light for a long time. Using regular absorption spectroscopy in the UV region suffers from interference problems. More recently, TDLAS has been successfully developed for the detection of trace levels of H₂S in natural gas. Commercial systems are now available that use TDLAS for measurement of H₂S, overcoming many of the interference issues.

V- FLUORESCENCE QUENCHING SPECTROSCOPY

Fluorescence is a photochemical process by which certain molecules will emit light of a different wavelength when illuminated by light (usually in the UV region). In this process, UV light “pumps” the molecules into a higher excited state, which then decays by giving out light. Fluorescence spectroscopy, by itself, has found many different applications in other industries.

WHAT IS QUENCHING

The intensity of the fluorescence can be reduced by the presence of different molecules that may be in the vicinity of the material. This reduction in the fluorescence emission is called “quenching”. The level of quenching will depend on the number of quenching molecules.

The main application of this method in natural gas analysis is the detection of oxygen molecules. Oxygen is a well-known and studied molecule that acts as a quencher. In this method, a known substance with a known fluorescence emission spectrum is illuminated, and the fluorescence emission is monitored. Depending on how many oxygen molecules hit the emitting material, the fluorescence emission is reduced. By measuring this reduction (quenching) one can determine the level of oxygen.

This method is particularly useful as Oxygen cannot be measured with IR absorption spectroscopy as it is a homonuclear molecule. It is subject to interference from other molecules; i.e. other molecules which may also quench the emission. However, these other molecules do not normally occur in natural gas. The fluorescence-emitting material will also degrade over time, and calibrations are needed to make sure the degradation does not cause errors.

VI- RAMAN SPECTROSCOPY

Raman Spectroscopy is a method by which molecules are excited into a higher vibrational state. As the molecule decays into its original states, it emits radiation based on the structure of its vibration states. Molecules have very distinct Raman spectra. Like IR spectroscopy, Raman spectroscopy can be used for the accurate determination of concentrations of molecules.

Figure (H) represents the schematic of the Raman Effect. The radiation source, usually a laser, is used to “pump” the molecules into virtual states, which will radiate back to the vibrational states of the original electronic state by emitting photons that are shifted by the separation of the vibrational states.

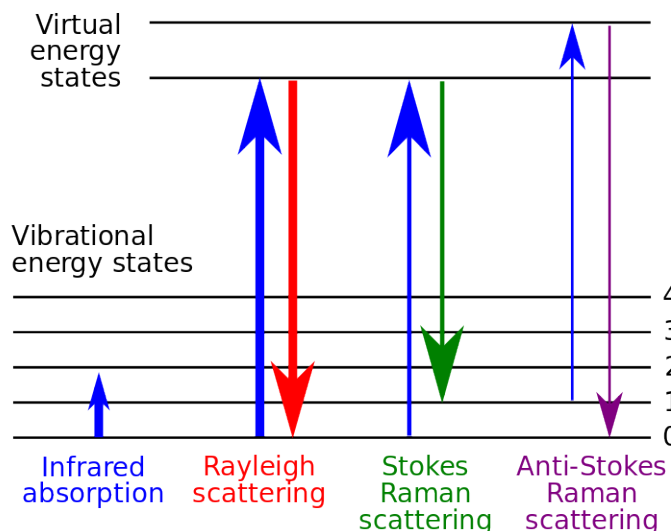


Figure (H) - Schematic representation of the Raman Effect

Figure (I) is a typical Raman spectrum. The Raman shift designates the frequency shift (or change in wavelength) from the original excitation laser frequency (or wavelength).

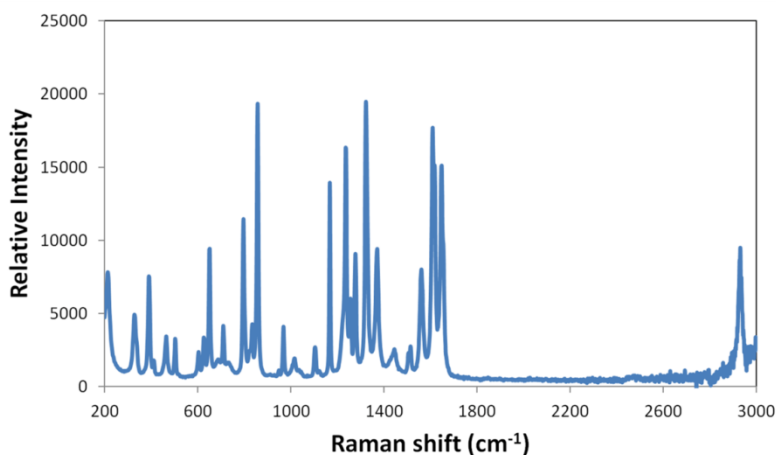


Figure (I) - A typical Raman Spectrum

Raman signatures are very characteristic of the molecule under analysis. There are spectral libraries with extended collection of Raman spectra for tens of thousands of molecules. Raman spectroscopy has two very important advantages over IR spectroscopy as well as a major disadvantage. The first advantage is that it can also detect homo-nuclear molecules. It has been used for measurement of N₂ in laboratory settings, though no commercial products are yet available.

The other advantage is that the wavelength of the original light source can be in principle anything. The emitted Raman spectrum will be close to the excitation wavelength. So one can pick an excitation wavelength where robust optical components are readily available at a reasonable cost, while minimizing interference from other effects. This usually means excitation wavelength from ~600nm-1200nm. Lasers and detectors in this range are very robust and low cost.

The major disadvantage of Raman Spectroscopy is its very weak signal. Therefore detection of trace elements becomes very difficult or requires high-power excitation lasers. In the gas phase, the density of the gas is already very low. Therefore detection of any trace components will be even more difficult and will require extended integration times to collect enough signal.

VII- CONCLUSIONS

Optical Spectroscopy methods are a collection of relatively old techniques, but are finding new applications in many different industries, including natural gas analysis. These methods are gaining increasing applications.

While optical methods have already become the gold standard for measurement of water, hydrocarbon, and water dewpoints, CO₂, and H₂S, other applications are emerging. For example, it is also very conceivable that Gas Chromatographs will soon be replaced with optical-based methods that will offer better reliability, no consumables and trouble-free operations.