

Module 7: Scattering Techniques

Lecture 42: Raman spectroscopy, fluorescence

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Fluorescence measurements

Under the influence of an external light source, outermost electrons of an atom undergo transition to the first (and possibly higher) energy levels of the material. On returning to the ground level, an electron is emitted with a frequency that corresponds to the difference in energy levels between the concerned quantum states. This frequency is, thus, purely a material property, independent of the wavelength of the incident radiation. Since the laser power required to raise electrons to the higher energy level needs to be necessarily higher, the incident frequency ν is greater than the emission at frequency ν_1 and scattering can be classified here as inelastic.

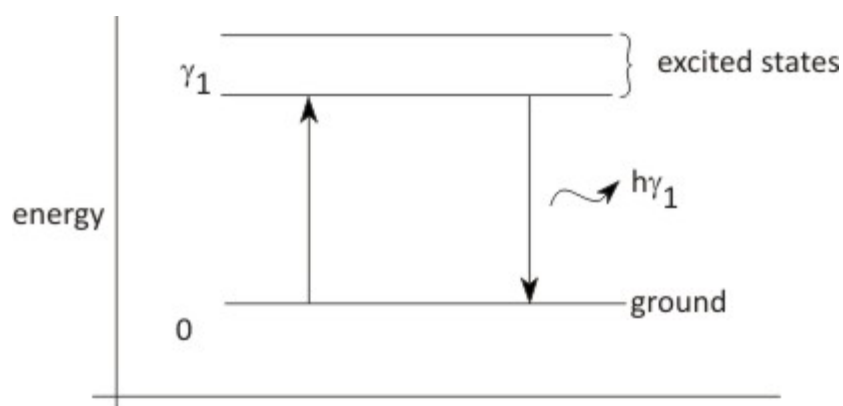


Figure 7.9: Energy transitions during fluorescence measurement.

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Fluorescence measurements (contd...)

A few considerations relevant to measurements are listed below:

- a. In gases, particulates may constitute the fluorescence medium. Fluorescent dyes can be added to liquids in small concentrations as markers. A laser sheet is invariably used to fluoresce these chemicals.
- b. The emission is usually in the visible range and a CCD detector can be used to record the intensity field. The camera is then aligned to image the plane of the laser sheet.
- c. Based on the discussion of Quantum scattering, regions of high intensity can be associated with regions of high dye concentration (also see Equation 7.5).
- d. The relative distribution of particulates/dyes in the flow field is a measure of the concentration field, and, indirectly the flow field itself.
- e. Fluorescence measurements invariably employ a tunable laser, such as a dye laser, so that the frequency of the incident radiation can be matched with the energy levels of the material under consideration.
- f. In practice, one uses a pulsed laser so that high intensities after scattering are possible. Higher laser power can help in detecting small concentrations of species, particularly in studies related to emissions in gases.
- g. The pulsing frequency can also be used to distinguish bonafide emissions from the background.
- h. Ideally, the laser wavelength is tuned so that the fluorescence output corresponds to a change in one quantum level and is, hence, monochromatic.
- i. In the event of multiple transitions within the material, a fluorescence *spectrum* is obtained. Such an output may be valuable under many circumstances.

For an example of fluorescence imaging, see movies 1-5 (*courtesy Dr. Arun Kumar Saha, Associate Professor, Department of Mechanical Engineering, IIT Kanpur*). These images show flow from a synthetic jet into a stationary fluid as a function of aspect ratio of a rectangular slot (movies 1 and 2) and nozzle diameter (movies 3-5). The frequency matches the resonance value of the piezoactuator. Synthetic jets take fluid from the surroundings and push them back with added momentum. The resulting flow is pulsatile and has applications in flow control and cooling of electronic equipment. For an introduction to synthetic jets, read [article 7](#) .

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Raman Scattering

Raman scattering is seen in materials composed of molecules (as opposed to single atoms as in monatomic gases). Here, the molecules may have rotational and vibrational modes of motion, apart from the translational. These modes are quantized and, as a result, all energy levels are split further into rotational and vibrational states. Specifically, the ground state is split as well, shown schematically in Figure 7.10. Thus, electrons may undergo transition from one of the higher ground states to the first energy level. After a certain residence time, these may return back to the true ground state. The difference between the two frequencies is proof of the *Raman effect*. In experiments, the frequency shift is the signal of interest and is material specific. Thus, Raman scattering is most commonly used for identifying species in a certain medium – solid, liquid, or gas. The intensity of the scattered signal is a measure of the number density of the species, and hence its concentration. If concentration is known, the signal can be used to determine pressure and temperature.

Raman signals can be expected from spontaneous emissions within the medium. Such signals tend to be very weak and stimulated emission is more often used in engineering measurements. The stimulant is the laser and one can detect Raman shifts in frequency with reference to that in the incident laser beam. Since Raman signals generally weak, a high power laser is necessarily required, adding to the cost of the experimental apparatus.

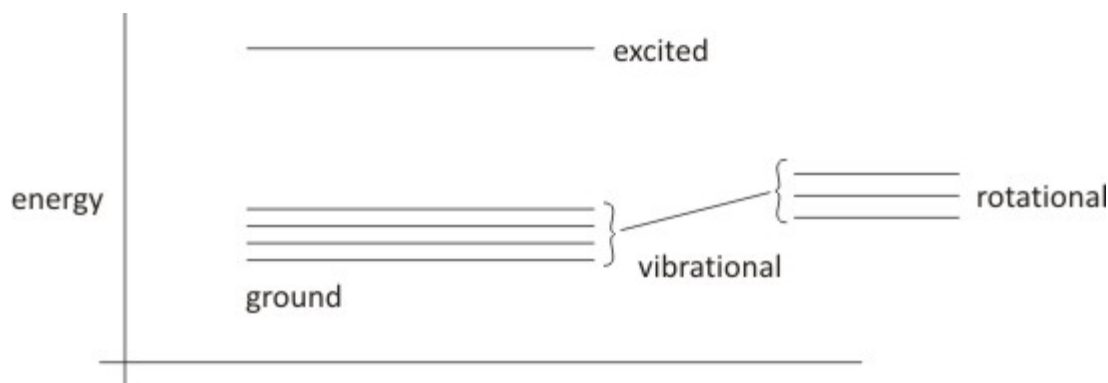


Figure 7.10: Energy states in molecules showing quantization of the ground state into vibrational and rotational levels.

When the emitted photon has a frequency less than the one absorbed, the frequency shift is called a **red** shift and is shown schematically in Figure 7.11 (left). When the frequency of the emitted radiation is greater than the one absorbed, one obtains the **blue** shift (Figure 7.11, right).

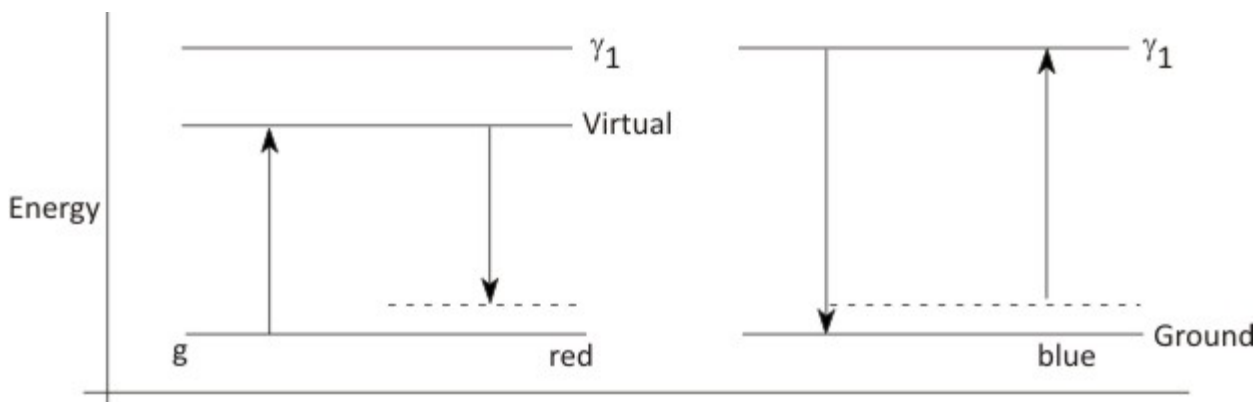


Figure 7.11: Schematic drawing of transitions in Raman spectroscopy. Left: red shift, also called Stokes red shift; Right: blue shift, also called the anti-Stokes blue shift.

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Raman Scattering (contd...)

An experimental set-up in which Raman scattering is utilized for species concentration measurement is shown in Figure 7.12. It has a high power laser as a light source. For steady state measurements, a continuous wave laser may be adequate. Unsteady fields will require a pulsed (Nd:YAG) laser wherein the pulsing frequency can be used to track transients. In addition, laser power is concentrated within a pulse and will help in stronger signal generation. The temptation to use high power lasers must be balanced against the possibility of melting (in solids), evaporation (in liquids) and formation of plasma (in gases). Raman signals may also be corrupted by fluorescence effects, making the choice of the laser wavelength a crucial parameter. Dye lasers are quite suitable from this viewpoint, since they are tunable with respect to wavelength. The laser beam can be focused to a spot using short focal length optics, thus enabling measurements of high spatial resolution. The optical components that collect the Raman scattered signal are physically large so that as much of a solid angle is covered as possible, around the point of measurement. Scattering is usually the strongest in a direction normal to the incident beam. The measurement of the scattered light spectra needs to be elaborate when a variety of quantities such as temperature and multiple species concentrations are to be jointly determined. The polychromator is an optical filter that can be tuned to a band width around each frequency where intensity needs to be measured. Intensity can be measured by a variety of devices such as intensified diode array detector, photomultiplier tube, or CCD cameras that have an added advantage of mapping a planar region. The measurement system is greatly simplified if only one quantity, such as temperature, is of interest. Here, frequency shift for the material undergoing scattering and the incident wavelength are both known. An interference filter can be conveniently configured for the measurement of light intensity in the concerned frequency interval. When multiple species concentrations are to be determined, the laser wavelength may be tuned to one molecule at a time. This would call for adjustments in the polychromator for appropriate filter settings. The synchronization of the light source, filters, and the light detector can be accomplished using personal computers with software such as labView.

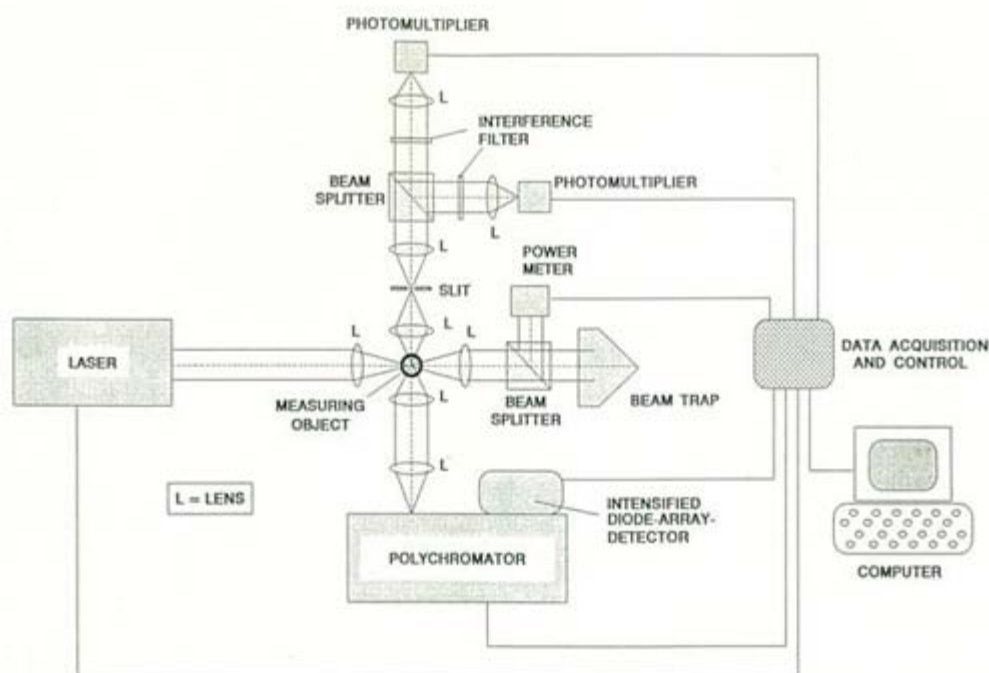


Figure 7.12: A laser-Raman experimental set-up for species concentration measurement, adapted from Mayinger (1994).

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Raman Scattering (contd...)

Typical Raman spectra, in the form of frequency shifts, are presented in Figure 7.13 for dry air (inhaled) as well as the air exhaled as human breath. Dry air is mainly nitrogen and oxygen, with traces of moisture (H_2O), indistinguishable levels of CO_2 , and other gases that the measurement has not been able to resolve. The intensity peaks depend on pressure, temperature and species concentration. Since the nitrogen content in air is an invariant and so is pressure, the nitrogen peak can be used to determine air temperature. With this information, oxygen levels in air being inhaled by an individual can be determined.

Note that Raman spectroscopy has determined concentration of all species in a single step; it points towards the power of the technique in engineering applications.

The second spectrum in Figure 7.13 is that of air exhaled. As expected it is rich in moisture and CO_2 , while the oxygen content has decreased. Nitrogen data can once again be used to fix temperature while other peaks will provide information on the respective concentrations.

Multiple peaks (such as CO_2 , Figure 7.12) are not uncommon. In fact, the identification of an intensity peak to a species is enabled by the vast amount of spectroscopic data available in the open literature.

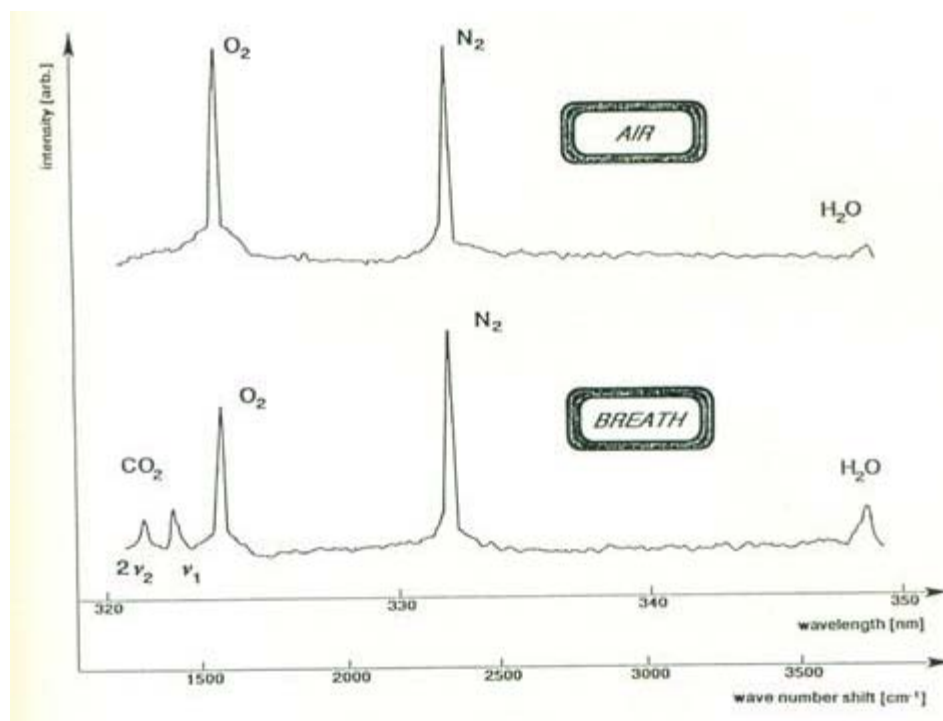


Figure 7.13 Raman spectra and species detection in air inhaled by an individual and air exhaled. Figure adapted from Mayinger (1994).

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Raman Scattering (contd...)

Figure 7.14 is an example where large changes in concentration are accompanied by significant changes in temperature as well. Here, hydrogen burns in air while the products of combustion include water, residual oxygen, nitrogen (that remains passive during the combustion process), and residual oxygen and hydrogen that remains unburnt through the flame. One can think of pressure as remaining practically constant (and equal to the atmospheric value) in the zone of investigation. Nitrogen peaks in the spectra can once again be used as signature of temperature. Note that the intensity diminishes with increasing temperature (for a given nitrogen concentration). This is understandable because the intensity values scale with the number density which, in turn, is inversely proportional to absolute temperature.

With reference to Figure 7.14, the hydrogen and oxygen concentrations are high, ahead of the flame. They progressively get consumed in the flame and reactions are complete behind the flame. Species concentration change in the zone of reaction. Beyond the flame, spectral changes will occur due to that in temperature. As expected, the concentration of H_2O after combustion is seen to be quite high.

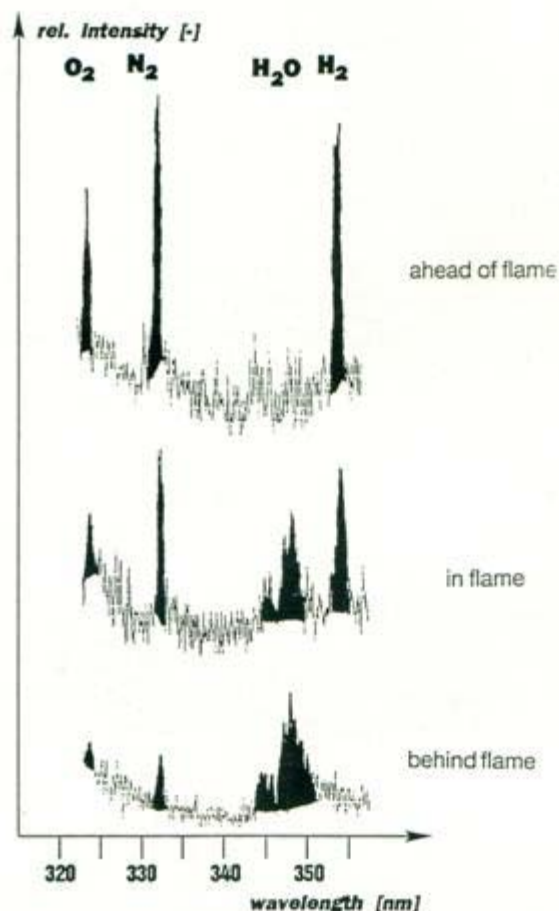


Figure 7.14: Raman spectra recorded in a hydrogen gas flame, hydrogen burning in air. Figure adapted from Mayinger (1994).

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Closure

The present module is a short introduction to optical methods that rely on photon-particle interaction and scattering for signal generation. Signals can be generated

- i. when the particle is large enough to cast a shadow,
- ii. particle influences the wave-like parameters of light, frequency and phase, for example, or
- iii. when the electrons are pumped to one of the (quantized) higher energy levels.

Correspondingly, signal strengths can be strong, mild, or very weak. The measurement costs are, in general, inversely proportional to the signal strength.

The connection between the signal intensity and the property to be measured has not been discussed in this chapter. The subject is quite vast and the reader is advised to consult the specialist literature on subject.

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