

Part IV. Fundamentals of Laser Spectroscopy

We have gone through the fundamentals of *atomic spectroscopy and molecular spectroscopy*, in which we emphasize the quantum physics and principles that govern the spectroscopy: why and how atoms and molecules form different energy levels or bands and different spectral lines or bands with different transition probabilities, polarization, angular distribution, shape, and width.

Atomic and molecular spectroscopy includes three major parts:

Theory of Atomic and Molecular Structures

-- Derive energy and angular momentum eigenvalues by solving QM eigenvalue equations under different internal and external interactions.

Theory of Radiative Transitions

-- Derive selection rules and transition probabilities by solving the time-dependent Schrödinger equation and analyzing wave function symmetry properties. This is part of the interaction between radiation field and matter.

Theory of statistical interaction of atoms and molecules with radiation

-- Combine the central frequency determined by atomic and molecular structure theory and transition probability determined by radiative transition theory with statistical behavior of an ensemble of atoms and molecules to derive spectral lineshape and linewidth. This is also part of the interaction between radiation field and matter.

These quantum physics and spectroscopy principles are mainly to answer the questions of why and how spectroscopy is formed in the observed ways. From microscopic world, we understand how various interactions inside an atom or molecule and interactions between an atom or a molecule with external fields determine the atomic and molecular energy level structures; how radiation interacts with an atom or a molecule to cause the radiative transitions of the atom or molecule between different energy levels or bands; how the observed spectral lineshape and linewidth are formed through the statistical behavior of atoms or molecules with radiation.

Through the class, we form a comprehensive understanding of the physics and principles and perform some quantitative calculations on the energy levels, transition probability and lineshape.

Now we turn our attention to another aspect of spectroscopy – the fundamentals of *laser spectroscopy*, in which we study the technologies and methods on how to detect atoms and molecules, how to obtain high detection sensitivity, and how to obtain high spectral resolution.

Laser spectroscopy is mainly to answer three major questions:

How to detect atoms and molecules using spectroscopy methods?

-- What physical or chemical effects can be used to detect and distinguish different atoms and molecules, from which density, pressure, temperature, and/or wind can be derived?

For example, based on absorption, the attenuation of transmitted light intensity, fluorescence excitation, photoacoustic effect, optothermal effect, optogalvanic effect, ionization effect, etc., can be used to detect atoms and molecules.

How to obtain high detection sensitivity?

-- How to minimize the threshold of detection intensity / concentrations?

Many smart ideas have been developed, e.g., frequency modulation, intracavity, cavity ring down, photoacoustic, optothermal, optogalvanic, laser induced fluorescence, velocity modulation, double resonance, optical pumping, etc.

How to obtain high spectral resolution?

-- How to “defeat” Doppler width or other broadening effects to distinguish fine and hyperfine structures of spectral lines, and to have minimum spectral linewidth?

Many smart ideas have been developed, e.g., saturation-absorption, polarization, atomic and molecular beam, cooling and trapping, Ramsey fringes, etc.

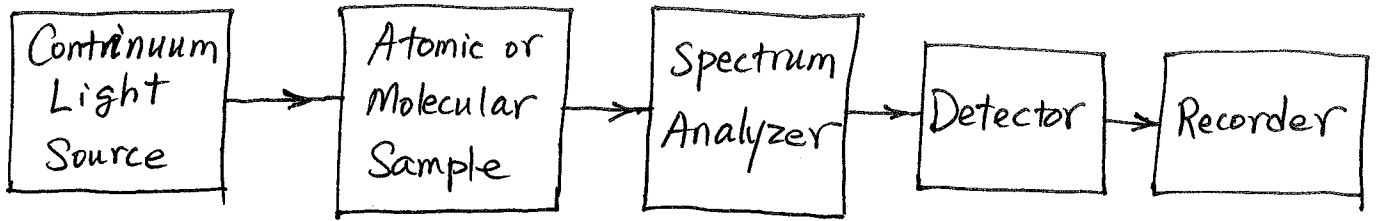
Laser spectroscopy is an important part of the interaction between radiation field and matter. These technologies and methods are based on the quantum physics and spectroscopy principles we learned earlier. Many laser spectroscopy ideas are developed for specific atomic or molecular energy level structures and radiative transition properties.

These technologies are constantly being improved, owing to the advancement of laser and detector technologies. These methods are so many that we cannot cover them all in our class but the textbook gives an excellent summary on these subjects, including both historic and recent developed technologies. In our lectures, we will emphasize the fundamental ideas of these technologies and set up a stage for students to further advance in the field in the future.

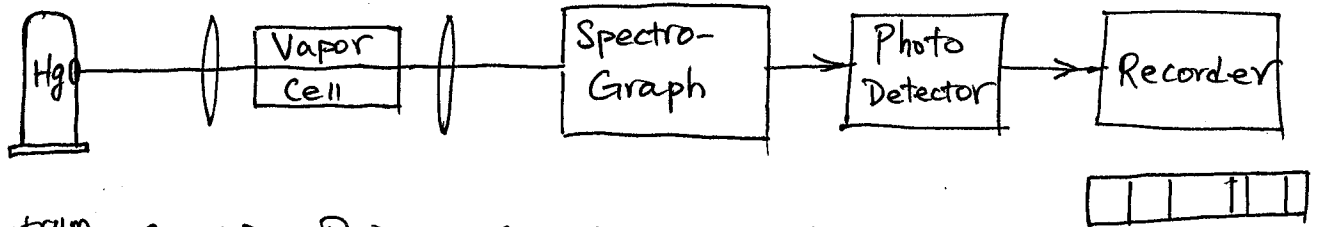
Chapter 13. Laser Spectroscopy Basics

13.1. Basic Setup for Spectroscopy Experiments

(1) With broadband light source

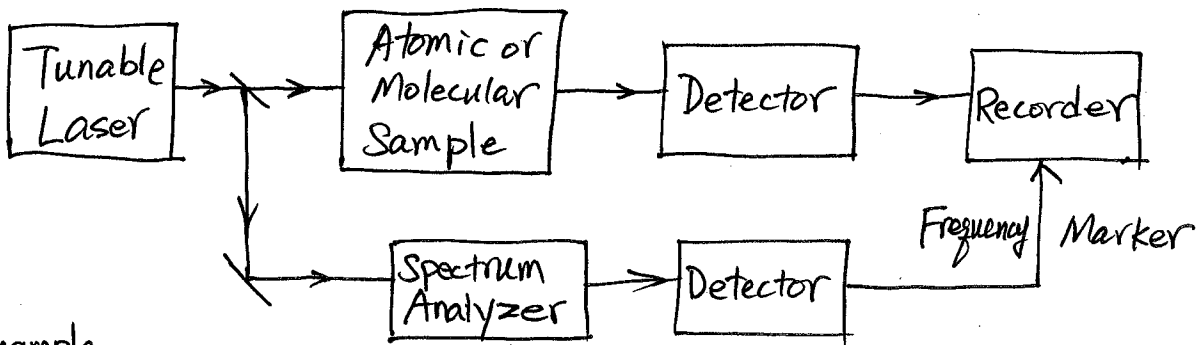


Example:

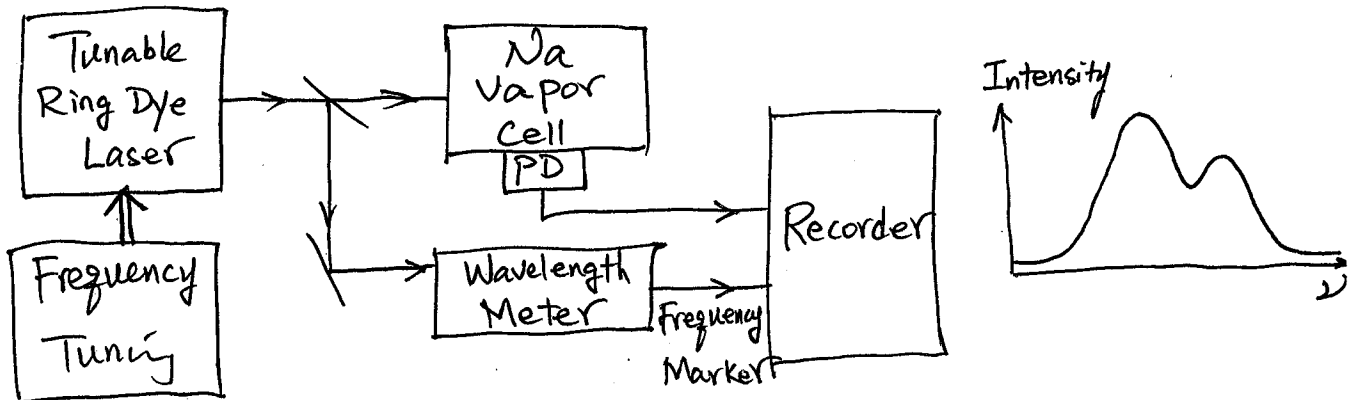


Spectrum Analyzer: Grating, Prism, Monochromator, FPI, etc.

(2) With Narrowband Tunable Laser as Light Source



Example:



- ① Light Source: could be spectral lamp, like Hg-lamp (+ filter)
could be lasers (especially tunable lasers)
could be sunlight or airglow or other natural source
- ② Atomic/molecular Sample: could be vapor cell
could be atomic/molecular beam
could be single atom or single molecule
in ion trap, laser trap, liquid, solid.
could be discharge gas lamp
- ③ Spectrum Analyzer: could be wavelength meter
could be etalon spectrum analyzer
could be grat \bar{g} , prism, FPI, (monochromator)
could be many other freq/spectra analyzer
- ④ Detector: could be photo detector like PMT, PD, CCD, etc.
could be pressure detector like microphone
could be thermal detector like bolometer
could be ion detector
- ⑤ Recorder: could be computer
could be film, photopaper
could be tape
could be oscilloscope

Light Source, Atomic/molecular Sample, Spectrum Analyzer, Detector, and Recorder are the five basic components of a spectroscopy experiment. No matter how complicated or how simple a spectroscopy experiment is, you can always find these five basic components, perhaps in different formats, in the experiment.

Actual spectroscopy experiments may have more components than the basic five, to different needs. For example, adding some filters to narrow down spectral range; taking beat signals between reference beam and signal beam; frequency modulation to improve signal-to-noise ratio; multiple pass of light inside the sample to increase absorption; chopping light for lock-in detection to improve SNR, etc.

In addition, the detector does not have to be behind the sample. It could be placed at many different positions, depending on the needs of experiment. For example, fluorescence detection prefers photo detector to be placed perpendicular to the laser light beam.

13.2. Basic Questions in Spectroscopy Experiment

How to detect atoms or molecules is equivalent to ask what kind of physical or chemical effect can be used to detect and distinguish atoms or molecules. In other words, what quantity is changed with and without the atoms or molecules investigated? or what physical quantity is changed when tune the laser frequency on and off atomic or molecular resonance spectral lines?

By detecting the change of certain physical quantity that is dependent on the sample presence or laser tuning, we can detect the existence of atoms or molecules, and distinguish their species by different spectroscopy signatures.

This comes to further questions: (1) to what sensitivity can the atoms / molecules be detected — i.e., the question of detection sensitivity; (2) to what resolution can the atomic or molecular spectra be distinguished — i.e., the question of spectral resolution.

These three questions are actually connected to each other:

① How to detect atoms or molecules?

② How to obtain high detection sensitivity?

③ How to obtain high spectral resolution?

Whether an effect can be used to detect ^{certain} atoms or molecules depends on how sensitive it can be and how high spectral resolution it can resolve.

Therefore, we cannot separate question ① from the other two questions. We will study question ① while studying the other two questions.

Even questions ② and ③ are also related to each other. But on certain aspects, they can be considered separately, as question ② deals with what effects are sensitive enough to be used to detect samples, while question ③ deals with how to "defeat" Doppler width or other broadening effects to distinguish spectral lines as fine as possible.

Textbook chapter 6 mainly talks about question ② while question ③ is addressed in chapters 7-14.

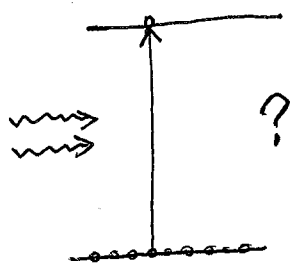
13.3. Basic Effects for Spectroscopy

IV8

Let us first summarize the effects commonly used in Spectroscopy so that we can have a big picture before going to details.

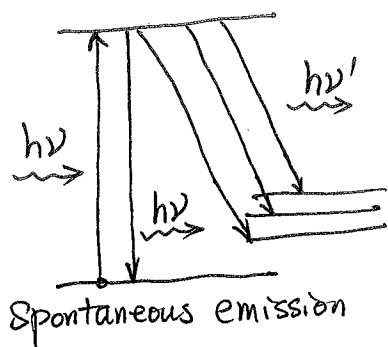
Majority of the spectroscopy methods are based on absorption of radiation by atoms and molecules, which is a frequency / wavelength dependent phenomenon. Some spectroscopy methods are based on Raman scattering of radiation by atoms and molecules, mainly for study of molecular vibrations and rotations.

Based on absorption of radiation by atoms or molecules, different effects caused by the absorption are utilized in various situations with various detection sensitivity. Just like the question we asked earlier: once atoms or molecules absorb radiation photons, what quantity or property of the sample or the radiation changes, which allows us to detect the absorption therefore, the existence of certain atoms or molecules?



To answer this question, we may consider what would happen after atoms / molecules absorb photons?

— Option 1: Spontaneous emission of photons while atoms / molecules decay back to the initial state or a different lower state.

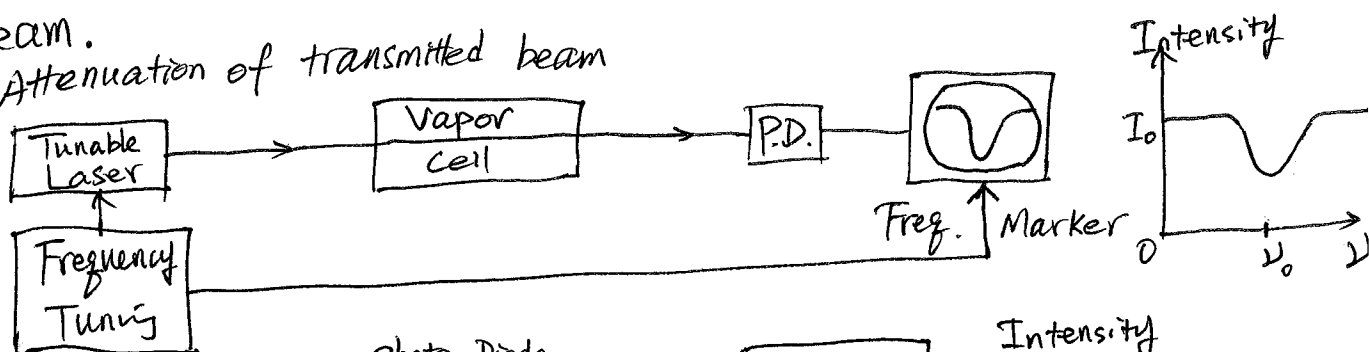


The fluorescence photons produced by the spontaneous emission can have the same frequency as the incident photon or different frequency, depending on the energy levels.

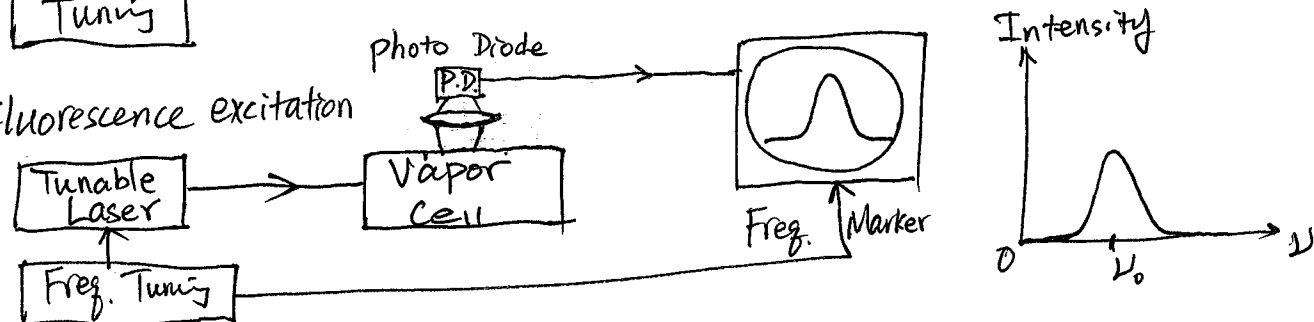
The spontaneous emission can go any directions, so it appears as a loss to the incident beam (because very small chance for the spontaneously emitted photons to go the same direction as the incident beam), while it appears as an increase of fluorescence to other directions, especially perpendicular to the incident beam.

From this, at least two effects can be utilized to detect the absorption of photons: one is the attenuation of the transmitted beam, and another is the increase of fluorescence in the directions different than the incident beam.

① Attenuation of transmitted beam



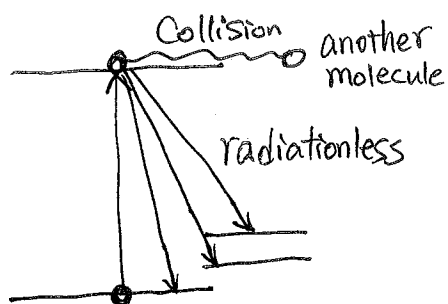
② Fluorescence excitation



For fluorescence to be produced, certain conditions must be satisfied. The key point is whether fluorescence can be produced and if yes, whether fluorescence can be collected.

- ① Quenching — collisional deactivation could compete with radiative transitions. Collision can cause radiationless decay of atoms/molecules to lower states. Quenching could occur when atoms/molecules are in high pressure conditions or in other way to say it — when collision rate is higher than spontaneous emission rate.
- ② Radiative lifetime of the upper states should be short so that (a) more probability to have spontaneous emission than collisional deactivation; (b) emit photons before atoms/molecules drift out of the observation period. Otherwise, even atoms/molecules emit fluorescence photons, they may not be collected by detectors. This could be a problem in molecular beam where interaction time is limited.

Usually, the upper electronic states of atoms/molecules have short lifetime (radiative), suitable for fluorescence detection as long as they are not under high pressure collision environment.

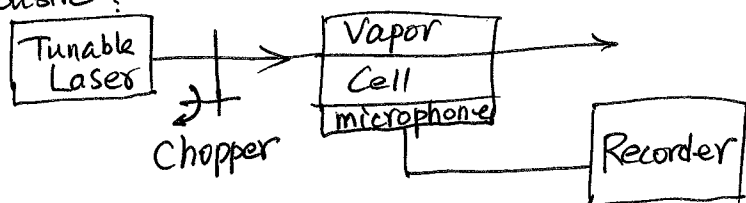


Collision with other atoms / molecules to transfer energy out

— Option 2. Collision with other atoms or molecules to transfer part or all excitation energy to the collision partners, while decay back to the initial or other lower states without emitting photons.

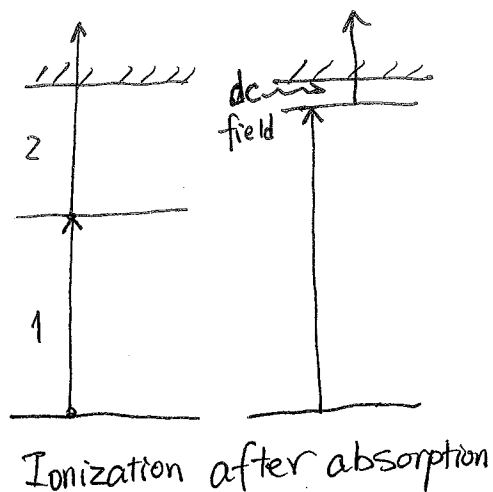
The conversion of excitation energy (i.e., incident photon energy) to the translational, rotational or vibrational energy of surrounding molecules will lead to the increase of thermal energy. Thus, it leads to a rise in temperature. For fix volume of vapor cell, the increased temp will lead to pressure increase at a constant density in the cell. — This is the photoacoustic effect that can be used to detect the absorption of photons.

Photoacoustic:



Of course, now the detector is not photo detector any more, but changed to sensitive microphone.

When the laser beam is chopped at frequencies $\Omega < 1/T$, where T is the mean relaxation time of the excited molecules, periodic pressure variations appear in the absorption cell. The output signal S of the microphone is proportional to the pressure change ΔP induced by the absorbed radiation power ΔW .

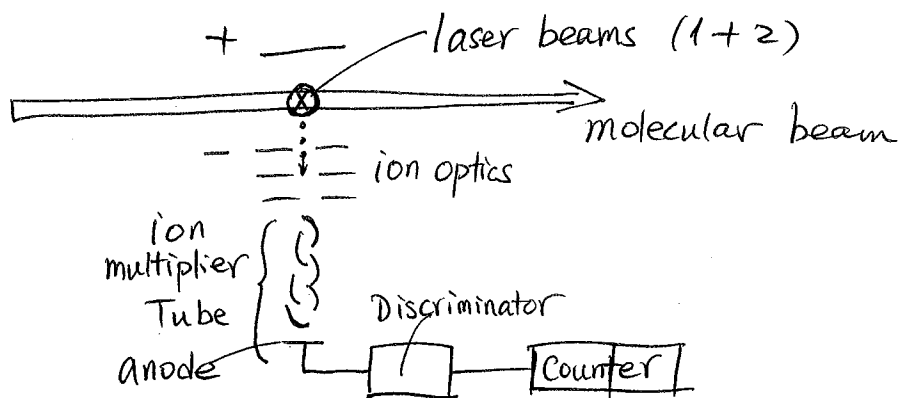


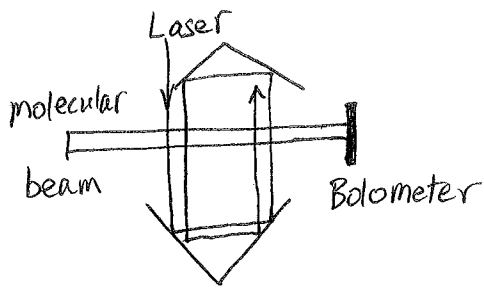
Option 3: after absorbing incident photon, atoms transit to an upper state. Then through other photon or collision or electric ac field, the excited atoms or molecules can be easily ionized. Thus, ions are formed.

By monitoring the ions or electrons produced by ionization of the excited atoms / molecules, the absorption of photons can be detected. — This is the ionization spectroscopy.

Of course, the detector is not photo detector, but changed to ion/electron detectors: ion/electron multiplier tubes.

Ionization:

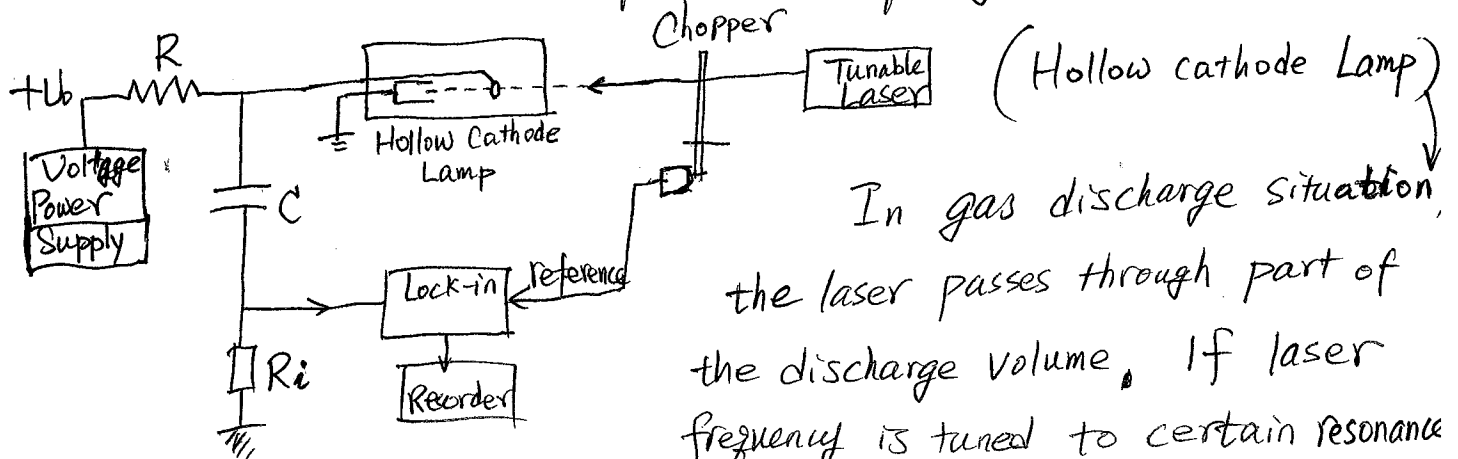




— Option 4. Optothermal effect.

When excited molecules strike the bolometer, they transfer the excitation energy to the bolometer, in addition to the molecules' kinetic and internal thermal energy. Thus, increasing the bolometer temperature by extra amount. By measuring the **heat** transfer rate, i.e., the temp change, the vibrational-rotational transitions in molecules can be detected, in the electronic ground state.

— Option 5: Optogalvanic effect.



In gas discharge situation, the laser passes through part of the discharge volume. If laser frequency is tuned to certain resonance

it will change the populations on different energy levels. Because different energy levels have different ionization probabilities, this population change will result in a change of the discharge current. This current change can be detected by measuring the voltage across resistor R . Thus, the absorption of photons is detected by the optically induced current change.

— Optogalvanic Spectroscopy.

In summary, based on absorption of radiation, the following effects are utilized for spectroscopy:

- (1) Attenuation of transmitted light intensity
- (2) Fluorescence excitation, including laser induced fluorescence
- (3) Photoacoustic effect
- (4) Optothermal effect
- (5) Ionization effect
- (6) Optogalvanic effect.
- (7) other effects

See Textbook Chapter 6

Each method has certain application range with the best sensitivity. It is important to understand each spectroscopy principles, applying conditions, advantages/disadvantages, detectors used, and techniques to improve sensitivity. Also, it is important to know the potential problems associated with each spectroscopy method.

Summarized in the following table is a comparison of these methods (incomplete). We are waiting for you to improve and complete the table. Actual application examples are wanted for each spectroscopy, which may be found in literatures.

IV15

Comparison of Different Effects in Laser Spectroscopy

Name of Effect	Nature of Principle	Application Conditions	Detector	Signal sensitivity
Direct absorption spectroscopy	Attenuation of transmitted light intensity		Photo detector like PMT, PD, CCD, etc	High background light Frequency modulation, intracavity, and cavity ring down can be used to improve sensitivity
Cavity ring down spectroscopy (a special case for direct absorption)	Measure the decay time of light passing through optical resonator filled with absorption sample	Multiple passes to increase absorption thus sensitivity		Optical heterodyne detection technique to enhance SNR
Fluorescence excitation spectroscopy	Spontaneous emission of photons	Atomic and molecular electronic transitions in UV, visible and near-IR for atomic / molecular vapor, beam, or single atom / molecule, etc (Not in high pressure medium where collision may deactivate fluorescence)	Photo detector, like PMT, PD, CCD, etc	Very low background Frequency modulation and lock-in detection can be used to improve SNR
Photoacoustic spectroscopy	Vapor cell pressure change caused by the collision-induced transfer of excitation energy into thermal energy	Vibrational-rotational transitions in molecules inside vapor cell (not in molecular beam)	Microphone to detect pressure change	Light is chopped to improve SNR
Optothermal spectroscopy	Bolometer temperature increase caused by molecule-bolometer collision-induced transfer of molecular kinetic and internal excited energy into thermal energy of the bolometer	Vibrational-rotational transitions in molecular electronic ground state in collision-free molecular beam with long lifetime (longer than flight time)	Bolometer	Laser beam is chopped to increase SNR by lock-in detection
Ionization spectroscopy	Ions or electrons produced by ionization of excited atoms or molecules after absorbing incident photons	In the case excited states lying close below the ionization limit	Ion or electron detector, like ion or electron multiplier tubes	
Optogalvanic spectroscopy	Optically induced discharge current change caused by the absorption of incident photons	In gas discharge – like hollow cathode tubes or lamps	Current or voltage meter	Light is chopped for lock-in detection to improve SNR

better SNR than Fluorescence? → PSD ←