

## A Brief Introduction to Diode-Laser Spectroscopy

The ideal spectroscopic experiment would involve illuminating a free and unperturbed atomic system with perfectly monochromatic light, and then seeing what happens, to the light and to the atom, as a function of the frequency of the light. And nowadays it's feasible for undergraduates to get hands-on experience of this very scenario in a tabletop, real-time experiment.

The nearly-ideal monochromatic light comes most conveniently from solid-state diode lasers, mass-produced for the needs of the optical data-storage industry. The first technology to be commercialized, using aluminum gallium arsenide (AlGaAs) semiconductors, led to the establishment of the near-infrared 785 nm standard for CD readout. Such laser diodes are physically small, and need only a DC power supply to produce useful ( $\approx 10$ -mW level) optical output. But astute physicists realized that the output wavelength could be varied by changing the laser's temperature, and further fine-tuned by changing the DC current operating the laser. Thus was born a wonderfully convenient spectroscopic light source.

To what atomic system might it be applied? Photons of wavelength 785 nm each convey an energy of only 1.58 eV, insufficient to excite most atoms from their ground states even to their lowest excited states. The exceptions are alkali metals, particularly rubidium (Rb) and cesium (Cs). In fact, rubidium's lowest excited states are split (by the spin-orbit interaction) into states accessible from the ground state by photons of wavelengths 780 and 795 nm.

Now these alkali metals are fiercely reactive to air or water, but compatible with glass, which brings up another convenience. A simple glass cell, evacuated and permanently sealed, with a bit of the solid metal inside, creates a great environment for spectroscopy. Light can get in and out through the glass, and (for temperatures in the range 20 - 50 °C) the metal will co-exist with its own vapor, in the form of a gas of freely-flying atoms of just the range of densities convenient for spectroscopic experiments.

Now it's time to imagine such an experiment -- what will happen when 785 nm light shines into such a cell? Answer: nothing at all; the light flies right through, because its wavelength is *not* resonant with rubidium atoms' allowed transitions at 780 and 795 nm. So the laser needs to be *tuned* to reach the resonant condition. In practice, this works through a hierarchy of mechanisms:

- 0) is to pick the right semiconductor;
- 1) is to hold the laser at the right temperature;
- 2) is to vary the current driving the diode-laser emission;
- 3) is to use a diffraction grating to create optical feedback into the laser, selectively for the desired wavelength;
- 4) is to use a piezoelectric element to tilt the grating ever so slightly.

In fact, mechanisms 2) and 4) are both electrically actuated, so it's possible to treat a working diode-laser system as a black box, with a variable control voltage going in, and a voltage-dependent optical wavelength coming out.

The application of a sawtooth waveform to this 'black box' will give an output beam whose optical frequency also undergoes a sawtooth in time, i.e. it scans up and down in optical frequency. And it's easy to accomplish the whole scan every 10 - 100 ms, so the laser's frequency is agile as well as variable.

Now it's rarely possible to get a diode-laser system to scan over any very long interval in wavelength -- even a scan from 780 to 795 nm for rubidium spectroscopy would be asking too much. In fact, it's time to think in terms of optical frequency instead -- such a scan would extend from 384,000 GHz down to 377,000 GHz. (Recall 1 GHz = 1000 MHz =  $10^9$  optical cycles per second.) In the simplest diode-laser systems, it's feasible to sawtooth-scan over only about 10 (not 7,000) GHz of optical frequency, which is only about a 30 part-per-million variation in frequency. Clearly, you want this relatively narrow scan to include the 780-nm target wavelength -- but once it does, what a wealth of spectroscopic information waits to be revealed!

How will it show up? The two mechanisms most easily displayed are absorption and fluorescence.

**Absorption:** that's the removal of energy from the beam of laser light as it passes through the cell. The exiting beam's power is easily measured, by conversion to an electrical current in a 'solar-cell' sort of photodiode, and it's easy to arrange a real-time oscilloscope display which shows transmitted power (on a vertical scale) as a function of the diode-laser's frequency-control voltage (a surrogate for its frequency, on a horizontal scale). Absorption will be indicated by a local *drop* in the amount of transmitted power. The process is easy to see, since fractional absorptions of 10 - 50% are easily achieved -- but only at the right wavelength!

**Fluorescence:** that's the production of light from inside the cell. For, if absorption happens, then assuredly energy is being removed from the light beam, transferred to the atoms as they are elevated to excited states. Since these atoms are in free flight in vacuum, there's no way for them to give up that energy except by 'radiative decay' -- they emit (in about 25 ns, on average) a photon of light in reverting to the ground state. These photons emerge in directions random with respect to the incident laser beam; in fact, a whole thread of atoms inside the cell, lying in the volume of the laser beam, *glows* as it emits into all directions this 'resonance fluorescence'. You can't see it by eye, only because your eyeball's sensitivity is so poor at these wavelengths. But simple solid-state CCD cameras have full sensitivity in the near infrared, so a monitor's display of the camera's view of the cell will image this fluorescence for you in real time.

One of the instructional pleasures of the diode-laser system is that the correlation of absorption and fluorescence can be seen in real time -- all that's needed is a slow scan in frequency over the resonance region, which will show that it's when (and only when) the transmitted power diminishes that the atoms are fluorescing.

But the next thing that appears in such scans, slow or fast, is that there are, as a function of frequency, *four* occurrences of absorption and fluorescence, not just one. This can be attributed to two causes:

1. There are two isotopes in natural rubidium, Rb-85 and Rb-87, and they have separate transitions frequencies.
2. Each isotope's atoms have 'two ground states', separated in energy by the tiny hyperfine interaction (the effect, on the valence electron, of the magnetic moment of the nucleus).

And, in fact, these ground-state hyperfine splittings are well known -- commercial rubidium atomic-frequency standards operate at the 6.834 GHz frequency corresponding to the energy difference between the two Rb-87 ground states. So that knowledge provides one way to calibrate the frequency scale along which the diode laser is being scanned. (There are direct optical methods for checking this calibration, such as unequal-arm Michelson interferometry, or the use of a Fabry-Perot resonator.)

Page 5 shows a detailed energy level diagram for the 780 nm, or D2, lines for both Rb-85 and Rb-87. The screen capture below it shows the transmitted power as a function of wavelength. You can match the "dips" to the transitions which caused them. (Our energy level diagram does not include the D1 transitions, which take place at 795 nm. They are the key to the phenomenon of Optical Pumping, another TeachSpin experiment.)

With a calibrated frequency scale, it also becomes clear that the four optical transitions you see are *not* infinitely narrow -- rather, they each have a 'spectral width' of about 0.5 GHz. In ordinary spectroscopy, such 'widths' are nearly always due to the imperfect resolving power of the spectrometer in question, but here it's not so -- the laser can be shown to be monochromatic to better than 0.01 GHz. So what is causing this width? It comes from the fact that the atoms being illuminated are *not* at rest, but instead are free-flying in vacuum. The relevant velocity is that component  $v_z$  of the atom's velocity along the direction of the light beam, because that motion causes a Doppler shift of the laser light's frequency. In the rest frame of the atom, the laser frequency is shifted from its lab value  $f_L$  to a received frequency of:

$$f_R = f_L (1 - v_z / c).$$

It is only when the received frequency  $f_R$  matches the atomic energy-level difference, according to  $h f_R = \Delta E_{\text{atom}}$ , that a transition will occur.

So a laser of fixed frequency in the lab frame will pick out only one 'velocity class' of atoms, namely the atoms having the  $v_z$  needed according to the equation above, and it will interact only with that class of atoms. Kinetic theory tells us how many atoms should have various  $v_z$ -values. In fact, there'll be a Gaussian distribution in  $v_z$ , with mean  $v_z$ -value of zero, but with mean-square value given by equipartition, according to:

$$(1/2) m \langle v_z^2 \rangle = (1/2) k_B T$$

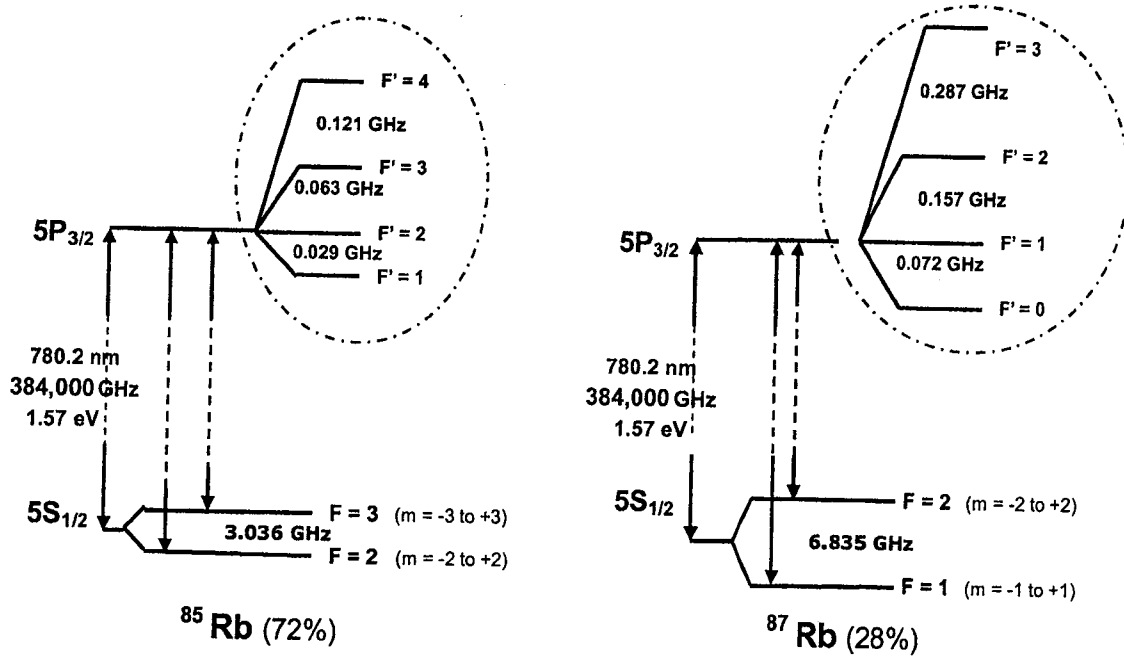
And that's why there's a Gaussian distribution in frequency, too, in the curve that gives the intensity of the fluorescence as a function of laser frequency.

Even here, the list of things to be observed spectroscopically is not nearly complete. Using the methods of laser spectroscopy, it is even possible to *surpass* the limits of Doppler broadening, and to achieve spectroscopic resolution far better than the 0.5-GHz Doppler width. The method involves splitting the laser beam into a strong 'pump beam' and a weaker 'probe beam', arranged to cross each other, at an angle of nearly  $180^\circ$ , at a location occupied by rubidium atoms. Now with milliWatt levels of optical power available, the pump beam is intense enough to cause a non-trivial depletion of the number of ground-state atoms in the particular velocity class with which it's in resonance. And the probe beam can sense this population depletion, as a decrease in the amount of absorption that would ordinarily occur. But that effect occurs *only* if the pump beam and the probe beam are interacting with the same sample of atoms; and because of the Doppler effect, that can only occur for atoms having  $v_z = 0$ . By this 'saturated absorption' effect, it's possible to resolve below the Doppler limit, and to see quantum transitions with a spectral width  $\Delta f < 0.01$  GHz. This is occurring at a laser frequency  $f \approx 384,000$  GHz, and so we can form a 'figure of merit' or quotient called the spectral resolving power, finding  $f/\Delta f > 4 \times 10^7$ .

Even at this superb resolution, it's *still* not the laser which limits the frequency width. Rather, the 'natural width' of the quantum transitions, related to the finite lifetime of the upper states, provides the next limit on resolution of  $\Delta f \approx 0.006$  GHz. But at this higher level of resolution, there's yet more to be learned about atomic structure. With the Doppler limit surpassed, it becomes clear that the atom's *excited* states also display hyperfine splittings, formerly invisible because of the Doppler broadening, but now cleanly resolved.

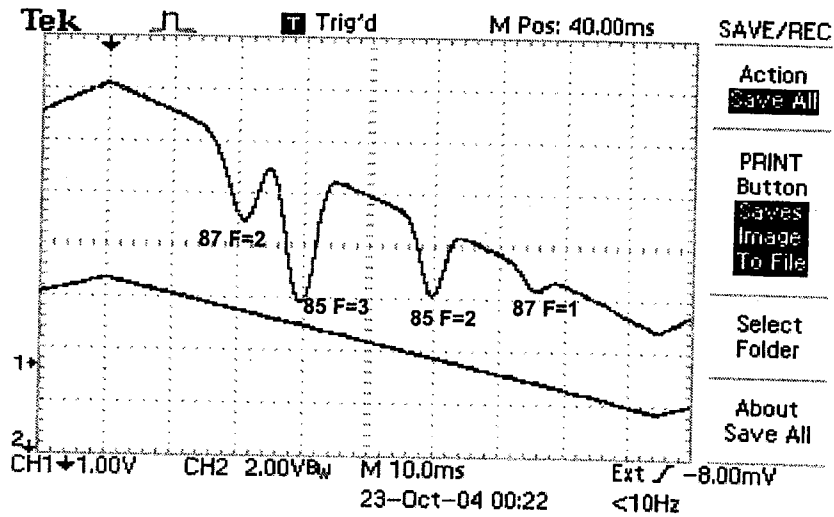
Lots more can be done on a tabletop scale. Given this ultrahigh resolution, for example, it's very easy to see the Zeeman effect of even modest magnetic fields further splitting the atomic energy levels. And beyond these simple experiments, very glamorous things have been done with diode-laser spectroscopy, including laser cooling, magneto-optical trapping, and even Bose-Einstein condensation. What's truly remarkable is how far along this path one can proceed on a *tabletop scale* and *with real-time accessibility* of the optical phenomena. And it is all made possible by the techniques of diode-laser spectroscopy.

## Rubidium Atomic Energy Level Diagrams



Energy Diagram shows D2 transitions only. The D1 transitions at 794.8 nm are not shown

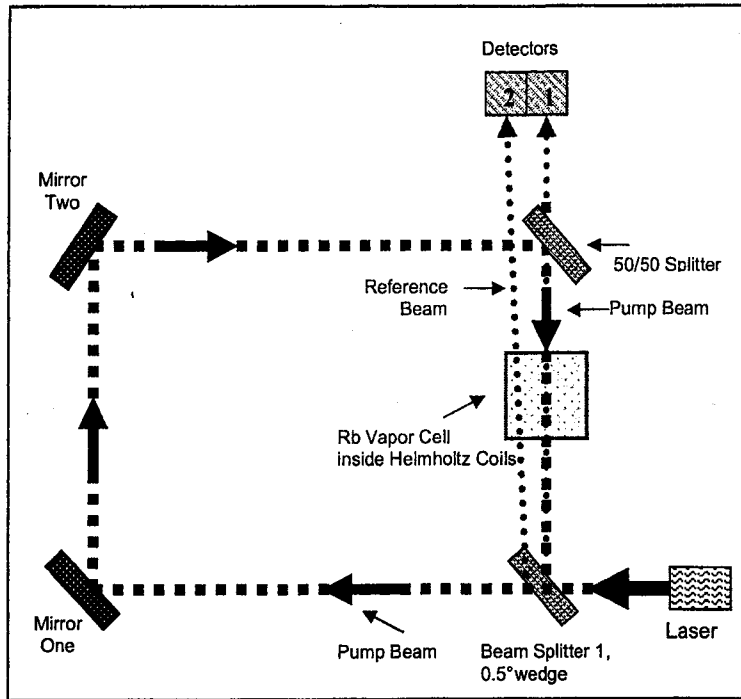
## Transmitted Light vs. Laser Frequency



Lower Trace: Sawtooth ramp voltage which is creating a “sweep” of both the laser current and the grating angle. This, in turn, creates the change in the laser frequency. Falling sawtooth indicates increasing frequency.

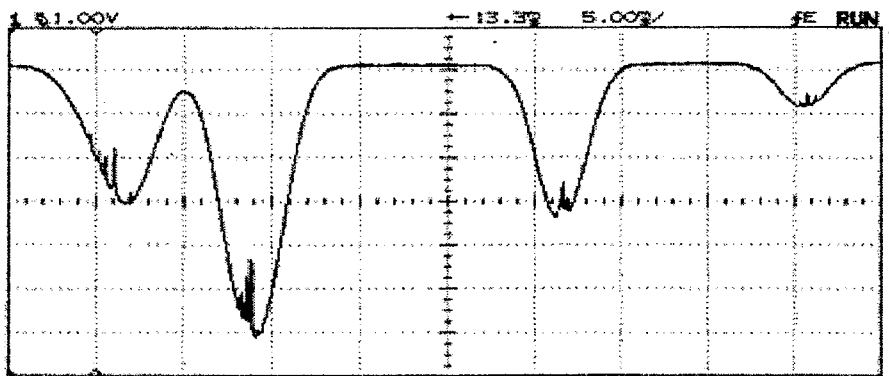
Upper Trace: Transmitted light received by the detector. In the section of the trace shown, frequency increases with time.

## Optical Plan for Saturated Absorption



A schematic diagram of an optical layout suitable for performing diode laser pump-probe experiments in rubidium vapor.

## Transmitted Light vs. Laser Frequency With Pump Beam On



Trace showing features that appear when pump beam is introduced. In the section of the trace shown, frequency increases with time. For this trace, only the grating angle is being changed. The laser current is constant, as indicated by the flat base line.

## Thinking about Saturated Absorption and Crossover Transitions

Barbara Wolff-Reichert – Rev 2.0 11/09

Any discussion of saturated absorption spectroscopy must begin with a reprise of the source of the Doppler broadening of absorption features. In absorption spectroscopy, a beam of laser light, which we will call a *probe beam*, is sent through a gas sample, in our case a mixture of  $^{85}\text{Rb}$  and  $^{87}\text{Rb}$  vapor, into a photodiode detector. The frequency of the light emitted by the diode laser is then modulated. As the frequency of the laser/probe beam sweeps through the frequency equivalent to the energy needed for a particular transition of the gas, photons from the beam will be absorbed and the atoms excited to a higher energy state. Of course, this energy is quickly reradiated as the atoms return to the ground state. The energy, however, is reradiated in all directions. This three-dimensional re-radiation creates a dual phenomenon – a line of fluorescence appears along the path of the photon beam and the intensity of light reaching the photodiode detector decreases significantly. For the TeachSpin Saturated Absorption experiment, the central frequency of the laser sweep is selected to stimulate a transition from the  $S_{1/2}$  to  $P_{3/2}$  energy state.

Were all the atoms at rest with respect to the beam, a graph of light intensity reaching the detector vs. the frequency of the laser would show a single sharp dip at the exact transition frequency  $f_0$ . The axes of an oscilloscope trace of photodiode detector voltage vs. time would be proportional to received light intensity vs. frequency and so would have the same shape. Because, however, atoms are in motion, atoms with a component of velocity toward the laser beam which we shall call  $-v_{ZA}$  will “see” the photons with a frequency  $f_A$ , which is actually an amount  $\Delta f$  below the transition frequency, as having a frequency  $f_0$ . These atoms will therefore absorb photons from the beam. In the same fashion, atoms moving away from the laser beam at speed  $+v_{ZB}$  will “see” photons of frequency  $f_B$ , (an equal amount above  $f_0$ ) as being at the transition frequency. As a result of this phenomenon, the oscilloscope trace we see is a wide, smooth, curve, a Doppler broadening rather than a sharp dip.

Figure 1 offers a way to visualize this Doppler process. In the upper section of the Figure, the vertical axis of the “graph” indicates the magnitude of a particle’s velocity in the direction of the laser beam. The horizontal axis is the frequency of the laser. The plotted line shows the velocity that a particle/atom must have in order to absorb the laser photons at that particular laser frequency within the sweep.

The lower section represents an oscilloscope trace of the detector signal vs. time as the frequency of the laser is swept from below to above the  $f_0$  transition frequency of our imaginary gas. The vertical axis thus indicates the amount of laser light reaching the detector while the horizontal axis indicates frequency. On an actual oscilloscope trace, the transition frequency would be hard to determine with much accuracy.

When using saturated absorption spectroscopy (SAS), however, the oscilloscope trace for atoms with a single transition shows a sharp spike within the Doppler dip when the laser frequency matches  $f_0$ . The process of SAS, like many great insights, seems obvious in retrospect. The laser beam is split into two unequal portions. The weaker portion, the *probe beam*, with only 10% of the initial intensity, is directed through the gas cell to the detector. The stronger or *pump beam* is directed around the cell and sent back through it, in the opposite direction of but collinear to the probe beam. The upper section of Figure 2 shows the z-velocity vs. frequency plot for particles that will absorb pump photons as a heavy line while the plot for atoms that will absorb probe photons is thinner. Notice that the two lines cross at  $v_z = 0$ ,  $f = f_0$ .

For most frequencies within the Doppler range, the pump and probe beams interact with groups of atoms moving in opposite directions. When the laser frequency is  $f_A$ , for instance, atoms moving toward the probe beam at a velocity we can call  $-v_{zA}$  absorb the probe beam photons. However, for the pump beam, it is the atoms moving at  $+v_{zA}$  which "see" the pump beam frequency as elevated to  $f_0$ . At this frequency, the presence of the pump beam has no effect on the amount of light reaching the detector. As the laser frequency sweeps through  $f_0$ , however, atoms with a  $v_z = 0$  can absorb photons from either of the beams. The stronger pump beam saturates the transition, leaving far fewer atoms to interact with the probe beam. As a result, the intensity of the probe beam light reaching the detector increases significantly, creating the sharp spike shown in the lower section of Figure 2.

But what happens if there are two or more closely spaced transitions, transitions so close that the oscilloscope signal appears as single wide Doppler dip? As Figure 3 indicates, for a case of two closely spaced transitions,  $f_{01}$  and  $f_{02}$ , the oscilloscope trace will show not two but three spikes within the Doppler curve. While two spikes are at the expected frequencies, the frequency of the third spike is exactly halfway between the two actual transition frequencies. At this "halfway" frequency,  $f_{12}$ , two groups of particles have velocities which allow them to absorb photons from either beam. Because of their motion, atoms with velocity  $+v_{z12}$  "see" the frequency of pump beam photons as elevated to  $f_{02}$  while the probe beam photons appear to have a frequency of  $f_{01}$ . For atoms of velocity  $-v_{z12}$ , the opposite effect occurs. For both sets of atoms, the absorption of probe beam photons decreases creating a spike in the Doppler curve.



## Doppler Broadened Signal

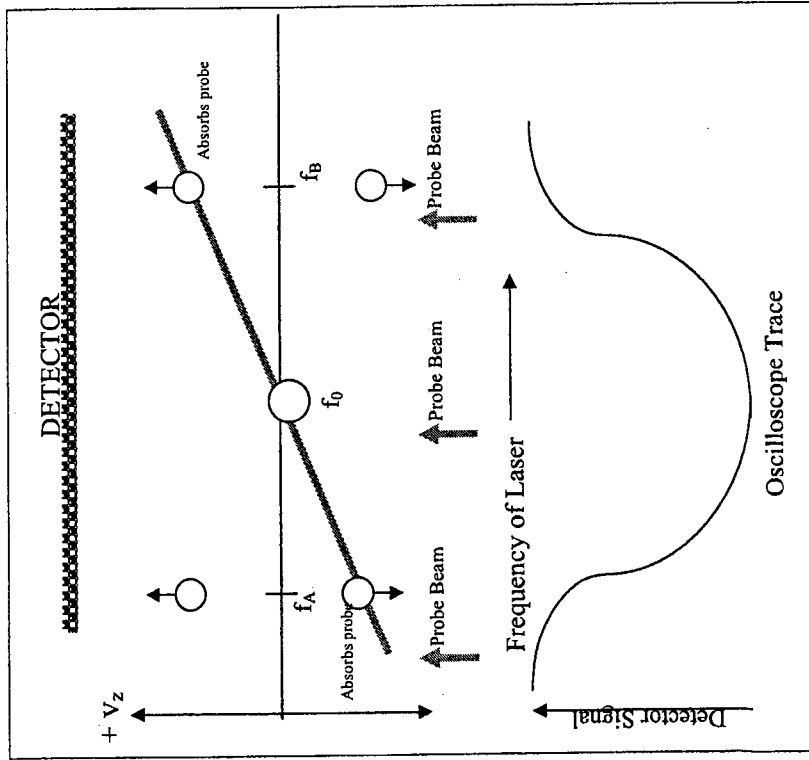


Figure 1

Doppler broadening occurs when the frequency of the laser is swept on either side of the "true" absorption frequency  $f_0$ .

When the sweep frequency is below  $f_0$  (as  $f_A$ ) probe photons are absorbed by gas particles moving towards the probe beam at a velocity which Doppler shifts  $f_A$  to  $f_0$ . When the sweep frequency is above  $f_0$ , probe photons are absorbed by particles moving away at velocities that "see"  $f_B$  reduced to  $f_0$ . When the laser frequency is  $f_0$ , particles at rest or moving perpendicular to the beam absorb photons.

## Saturated Absorption

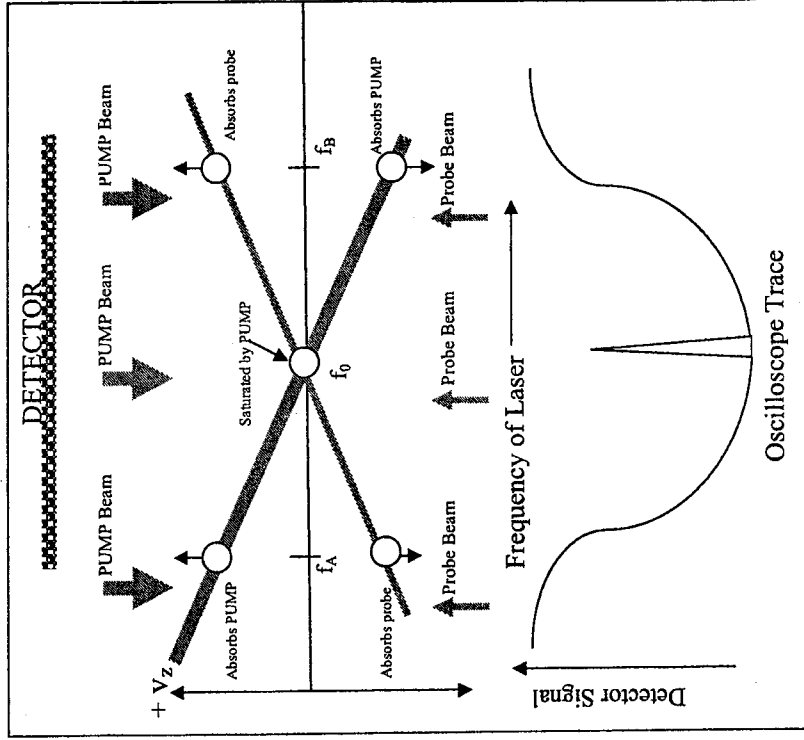
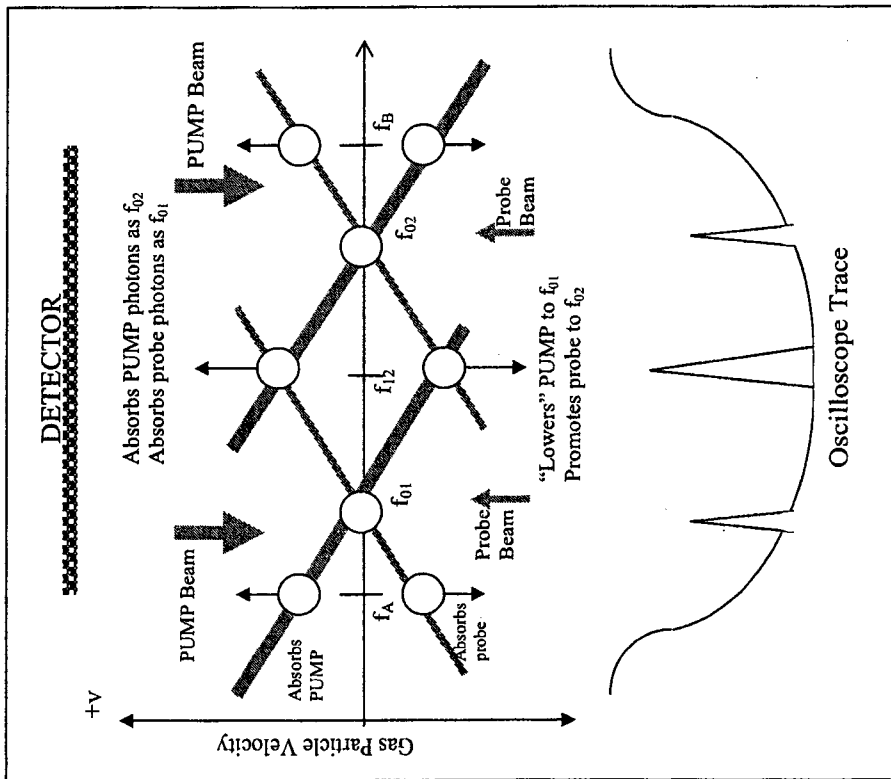


Figure 2

At frequency  $f_A$ , (below true absorption frequency  $f_0$ ) probe and pump photons are absorbed by particles moving towards the each beam. These are completely different sets of particles so the probe signal is unchanged. With the laser frequency at  $f_B$ , which is above  $f_0$ , photons are absorbed by particles moving away from each beam.

When, however, the laser frequency passes through  $f_0$ , particles at rest or moving perpendicular to the beams can absorb photons from either beam. The PUMP beam 'saturates' the transition. Since fewer particles are available to absorb probe photons, the intensity of the probe beam reaching the detector is increased and the signal "spikes".

## Crossover Transition



When a transition can be made from the ground state to two upper levels, adding the pump beam creates three "spikes" within the Doppler curve. Increases in transmission occur, as expected at the two actual absorption frequencies,  $f_{01}$  and  $f_{02}$ . The third spike, called the "crossover" transition, occurs exactly halfway between the two. At this frequency, an atom moving with the proper velocity in the  $+v_z$  direction can either Doppler shift the probe beam photons down to  $f_{01}$  or the pump beam photons up to  $f_{02}$ . Thus at this crossover frequency  $f_{1/2}$  the atoms available for absorbing probe beam photons is reduced. More probe beam photons pass through the vapor and the detected intensity rises. Similar reasoning describes the fate of atoms moving at the proper velocity in the  $-v_z$  direction.

When three possible transition frequencies fall within a Doppler curve, as in our rubidium vapor experiment, six spikes are produced. In addition to spikes at  $f_1$ ,  $f_2$ , and  $f_3$ , there will be crossover spikes at  $f_{12}$ ,  $f_{23}$  and  $f_{13}$ .

Figure 3