My name's Joel Hales I'm a research scientist here at Georgia Tech in Professor Perry's group and today we're going to be talking about femtosecond z-scan. So this is a technique which is used to characterize third-order nonlinear optical materials.

So the linear optical properties of materials are characterized by there on first order susceptibility or chi (1) and these are responsible for optical properties like the refractive index and the absorption coefficient. So we use pretty typical techniques to characterize them like absorption, spectroscopy ellipsometry, prism coupling and things like that.

However, when you start increasing the amplitude of the optical field that is applied to materials they tend to respond nonlinearly. And so then we start getting into a higher order effects and those can be characterized by the second-order susceptibility which is responsible for things like the electro-optic effect and second harmonic generation. What's interesting in second order-materials is that they have to have an intrinsic asymmetry associated with them in order to exhibit any type of response.

That's not true with third-order materials. As a matter of fact there aren't any real restrictions for what gives rise to third-order materials in terms of symmetry so third-order nonlinearities are present in all materials.

That makes it interesting from the perspective of doing applications because just about any material is a potential candidate. So what we want to do today with this setup is be able to characterize the third-order nonlinear properties of materials. They're related a lot like chi (1) is to linear materials. There is a nonlinear refractive index and a two-photon coefficient.

So those are the types of effects that are being used to do applications such as all optical switching and frequency conversion as well as all of these two-photon absorption type applications like bioimaging and multi-photon lithography. Z-scan is a remarkably easy technique to set up and has a very simple layout.

So we simply monitor the transmission of a focused Gaussian beam through a sample and by monitoring that transmission we can get both the nonlinear refractive index and the two-photon absorption coefficient.

So it's very unique in the fact that you can look at a number of different types of samples. You can look at solutions and films. You can look at highly absorbing materials, non-fluorescent ones, so it's very amenable to that. It has its drawbacks; you have to do it more or less a single wavelength at a time it can be a little bit tedious. It doesn't have any temporal discrimination for instance like transient absorption might.
But despite all those drawbacks it can be used to characterize a number of different materials.

Our optical source is an amplified femtosecond laser which actually goes into an optical parametric amplifier and that is what allows us to tune the wavelength of our excitation. So right now we're working at 640 nanometers which is in the red.

So we have the beam coming across the table to this mirror here. We actually have it coming down to this mirror here and it's going into an attenuator and this allows us to control the intensity of the beam when we're doing our measurements, and it’s computer controlled.

After we pass through the attenuator we go into what's called the spatial filter and the spatial filter allows us to clean up the beam that comes out of the parametric amplifier which is typically not of a good quality and we need a very high quality beam in order to do z-scan.

So what the spatial filter does is that simply focuses down the beam to pinhole and that pinhole allows you to cut out the higher spatial frequencies of the beam. So the beam that actually comes out doesn’t have these higher spatial frequencies which leads to a poor beam quality.

So after we go through the spatial filter we collimate the beam and we travel down the table and we actually enter into the z-scan apparatus. So after the beam bounces off a couple of mirrors we actually come into the z-scan technique here. And a portion of the beam is actually sampled by a reference detector and that's going to allow us to account for fluctuations in the energy from pulse to pulse.

It’s going allow us to quiet down the actual signals that we get by taking the ratio that detector to the detectors we’re going to look at in a few seconds. So the beam travels down this path here it goes into a simple focusing lens and then this lens actually focuses the beam into the sample. In this case what we have in here right now is a semiconductor zinc sulfide it's about two millimeters thick. And so we actually have it focusing slightly past the sample here and then spans until we go into another filter wheel and then it actually gets split up between two detectors.

One detector just goes along that same path, we collect the light and we focus it into the detector, and the second detector is at the exact same type of geometry with one exception there's an aperture in it. And so what we’ll refer to these two arms as the open aperture or no aperture and the closed aperture this is going and be important because the two types of properties that were trying to analyze in these third order materials are the nonlinear refractive index and the two-photon absorption coefficient .

So the open aperture arm is going to be sensitive to two-photon absorption and the other arm will be sensitive to both but through a little bit of math we will be able to actually extract out the nonlinear refractive index from the closed aperture arm.

So to try and explain how this works it's a little bit easier to start with two-photon absorption since two-photon absorption is actually dependent upon the irradiance that you are exciting with. As you actually focus down tighter your irradiance gets larger, and so your two-photon absorption should also get larger.

So what happens is as we move this sample from where it's not focused to where the beam is focused we should get an increase in nonlinear absorption and that's what we're going to monitor on the open aperture.

It's a little bit more complicated in the closed aperture arm because what we're measuring is a type of refractive index again the nonlinear refractive index increases as you get to higher intensities.

That works like a lens and so what happens is if you have a sample that has a positive nonlinear refractive index it effectively makes the beam focus a little bit shorter than it originally did which means that by the time it gets over here less light is getting through this aperture.

Consequently as you go through the focus what'll happen is the actual material will start to refocus the beam and more light will go through the aperture. And so what will happen and we'll see this on the computer screen in a second, is you’ll get an oscillatory behavior to the signal. And by monitoring the transmitted beam in the open aperture arm and the closed aperture arm we should be able to extract out the two-photon coefficient and the nonlinear refractive index.

So what we're observing here are the detector voltages from the three detectors I showed before. This is the reference detector that comes before the actual focusing lens. This is the open aperture or no aperture arm, and this is the closed aperture arm. The rest of these columns are simply taking the ratio of one voltage divided by the reference and again that's just to make things a little bit quieter. You can see the numbers that are appearing in these columns seem to be fluctuating a little bit more than the numbers in these columns. Effectively we’re just taking out the pulse to pulse instability of the laser system.

So what we're going to do now is actually run a z-scan. A z-scan just consists of monitoring these voltages as you move the sample through the focused beam. So here we're actually going to put in the parameters for the experiment. Here we can put in the number of pulses that we're going to average for each individual group, and the group basically consists of a particular position of the stage as you’re moving the sample through the beam. So we're going to do a hundred groups and this just tells you that for each group we’re going to move in millimeters steps.

So we go ahead and name the file we’ll bring up the actual acquisition program, and acquisition program as is showing here you can actually see the ratios that were shown on the previous screen. Here you're going to get the open aperture signal in the green you're going to get the closed aperture signal and that we're going to divide the two.

So again the open aperture signal was sensitive to two-photon absorption so as you get closer and closer to the focus, which is going to be right around fifty here, you're actually going to see that transmittance drop again because there's nonlinear absorption occurring. And it will look symmetrical about the axis. The green curve here is the closed aperture. It is sensitive not only to nonlinear absorption but also nonlinear refraction, and say you actually see a dip that's kind of reminiscent of the open aperture scan but you kind of see a slight asymmetry.

It turns out in some samples if you divide one by the other you can get what looks like the nice symmetric dispersive curve and by fitting that we can actually get the nonlinear refractive index.

So once we actually have the data from the experiments we can use a fitting routine which was defined in the originals z-scan paper some twenty years ago, and we can use the experimental parameters that we've measured before. In order to do this we need to be able to accurately measure what the irradiance is. It means that we have to take great care in measuring the energy of the pulse, its pulse width, and its beam size.

So those are things that we do prior to the actual experiment and we can input these parameters up here along with a number of different sample parameters such as sample of path length, linear transmittance, linear refractive index and some other things. And then we can go ahead and run this program and what you can see here in the upper left hand corner are those three curves that you saw when we were actually running the experiment. Again the red curve here is the open aperture, the blue curve is the closed aperture, and the green is the division of the two.

And so what I'm showing over here is our ability to fit that open aperture data. By fitting it we can extract out the two-photon absorption coefficient. By doing the same thing to this divided scan we can get the nonlinear refractive index. And that's and that's how we characterize our particular material.

So z-scan allows us to characterize the third-order properties of a number of different materials. So far we've been talking about bulk materials but what you can do is if you take a solution of a known concentration of an organic molecule you can actually extract out the molecular parameters that are associated with the nonlinear refractive index and the two-photon absorption coefficient. And so this can allow you to do structure - property relationships where you effectively characterize the molecular parameters, you change the structure, and see how one affects the other.