[SQUEAKING]

[RUSTLING]

[CLICKING]

**JOHN DOLHUN:** Hello. Good afternoon, everyone. And welcome to the second to the last lecture. Next week, the X-ray diffraction, Peter Mueller will deliver that, I believe, on Tuesday.

And this is the mass spec lecture, and then we'll keep you posted as what happens in between. There are a couple of workshops for the oral reports, and we'll also have a couple of town hall meetings, one of them being, I believe, next week, next Thursday, which will cover all three of the labs that you're working on. You can come here with your questions and computers and calculations, and all the TAs and both instructors will be here to help you navigate through the third lab.

So today, I'm going to talk about mass spectrometry. And J.J. Thompson, discoverer of the electron, won the Nobel Prize in 1906 in physics, but not for the discovery of the electron, for the conduction of electricity through various gases and discharge tubes. And then, after he won that Nobel Prize, seven members of his research group won Nobel Prizes. And then, in 1937, his son won a Nobel Prize for figuring out the wavelike properties of the electron that his father discovered. Nine Nobel prizes in one research group. It's just amazing.

So J.J. went on to build the first mass spectrometer in 1912. And in honor of him, we're going to do a little electrical demo, just to start off with you today. So what we're going to be doing is I'm going to be showing you an incandescent light bulb. And you all know them. This is a big version. This is the small version.

Inside of the incandescent light bulb, there's the filament. And they've used tungsten since the turn of the century, the turn of the last century, 1906, because tungsten has the highest melting point of all the metals. Melts at around 3,400 degrees Celsius.

So inside of there, you can see it in this bulb, but I'm just going to turn this on, just for a moment. So you all know the incandescent bulbs. They get so hot.

When the electrons flow, they flow through the circuit, and then the tungsten atoms start to vibrate inside and it heats up to about 2,200 degrees. Have any of you ever touched one of these? You do it only one time because they are so hot, and that's why they're so wasteful of electricity. That's why we're going to the LED lights today.

But what I've done here is inside of that light bulb and this bulb, there is an inert atmosphere. There's argon and nitrogen gases to protect that filament. If they weren't in there, I scratch my head and I'd wonder what would happen to that filament.

So what I did is I took a bulb here and I'm going to break one. Hold your ears. And out-- oh, beautiful. The filament's completely intact. See, I didn't break it.

But I've already got one here to show you this demo with. So what we're going to do is I am going to take one of these filaments outside of the light bulb and I'm going to turn on the electricity and see what happens. Let's turn the lights down now. Yeah. And he just shut this light off here. You ready?

**AUDIENCE:** Whoa.

**JOHN DOLHUN:** Wow, didn't take long, right? In the oxygen atmosphere, the electrons are flowing through there and the tungsten atoms are boiling off with the electrons and the thing just disintegrates pretty instantly. So I said to myself, I want to do one more experiment. And Amanda's going to assist me with this.

We're going to fill this beaker with liquid nitrogen and we're going to take one of these filaments and we're going to stick it down into the liquid nitrogen and then we're going to turn it on. So think about that for a minute. What do you think is going to happen?

**AUDIENCE:** [INAUDIBLE]

**JOHN DOLHUN:** Go ahead, Amanda. I just blew one. OK. OK. All right. I ruined one, sorry. I forgot this was on.

OK. All right, let me turn this off for a minute. And I think I can put in the one that I took out here on the desk. I'm going to put that one in because the filament is intact. OK, Amanda. Just tighten it a bit. Go ahead. You OK?

**AUDIENCE:** Yeah.

**JOHN DOLHUN:** Liquid nitrogen, minus 196 degrees Celsius. Beautiful stuff. Put your finger in there and you know what's going to happen. It's the skin effect. Won't get you for the first few seconds.

OK, good. So here we go with our experiment. That's good, Amanda. So we're going to lower this down in. Amanda, do you want to hold this?

**AUDIENCE:** Sure.

**JOHN DOLHUN:** Just try to get it in the center and just lower it all the way down in.

**AUDIENCE:** All the way?

**JOHN DOLHUN:** All the way. Just go ahead. Take it down. Leave more slack. Yeah. Let it go down in. OK, good. Ready? There it is in the liquid nitrogen. Is it burning out?

**AUDIENCE:** No.

**AUDIENCE:** No.

**JOHN DOLHUN:** No. Take it out, Amanda. Doesn't take long in the air, does it? So even the liquid nitrogen is surrounding that filament and protecting it. And you've got the situation where you don't have the oxidation that's going on.

OK, so we take the lights back up. So in case you're interested, tungsten it had-- anyone read Oliver Sacks book, *Uncle Tungsten?* It's a great book. You've got to get that.

Tungsten plus oxygen goes to tungsten oxide. And you can actually-- if you take one of these filaments that burned out, you can actually see the yellow-white powder that from the tungsten oxide that was left over. So J.J. Thompson, because of his discovery of the electron, I wanted to show you this electrical demo. And now, we're going to get into the mass spec, which is pretty important because you're going to be using the mass spec to characterize your ester products in this lab.

So the inside of the mass spec has several basic components. You've got an area outside here that is at atmospheric pressure, and the area inside that is under a high vacuum. Anyone have an idea why that area is under a high vacuum inside? No?

So you're generating ions. The ion are going to get generated in this source. The filament is going to shoot electrons onto your molecule and it's going to ionize your molecule, and then the molecule's going to break apart. And positive ions are very short-lived species, so we manipulate them under vacuum.

And the vacuum-- the vacuum actually is great because it allows us to let the ion have a mean-free pathway from the ion source to the detector without any biomolecular collisions. So the ions are generated here and then they go into the mass analyzer and they're sorted by their mass to charge ratios, and then they're counted at the detector, and out comes a spectrum. You kind of get something like this with abundance here and the mass to charge ratio.

And depending on the iron, so you might-- the detector may see a lot of this, less of that and less of that. So you're going to get vertical lines representing the abundance of the ions that were detected in that spectrum. Each vertical line represents an ion. And we're talking about mass to charge ratios, the charges are usually plus 1. So what we're looking at in a mass spectrum are the masses of the individual ions.

Mass spec is-- the basic principle of mass spec is you have to have an ion that enters the magnetic field and it gets deflected. It gets deflected dependent on the actual mass to charge ratio, how big that system is. Bigger, heavier atoms are going to be deflected less than small, lighter atoms. But that's the whole underlying principle of mass spectrometry.

And now, I'm going to talk about a couple of the types of ionization. Electron impact is the basic form. So what we have is we've got our molecule and we send it into the ion source. It gets bombarded by electrons, and you create an ionized molecule, an M plus dot.

And this ionized molecule can do one of two things. This could break apart. So the positive charge could be retained on one part of it. The radical would be retained on the other. So you could get something like A plus plus some radical given off.

Or it could break apart. So one part retains both the plus and radical. So you could get this type of ion and a neutral molecule given off. What we detect with mass spectrometry is we're detecting these daughter ions here.

These are the peaks we see. We don't see the radicals or the neutron molecules, but we could figure them out by subtracting the fragments from the molecular weight. And then we can-- we'll know what's been lobbed off.

So if you have a molecule like this, it could ionize anywhere in this chain. And if it ionizes, say, here, and then you have a homolytic cleavage of the bond, you're going to get an R prime CH 2 plus fragment, and you'll get an R2 CH2 radical. So that's the idea.

Now, sometimes, some of these bigger molecules, these proteins and peptides, you don't see molecular ion peaks in the mass spectrum. Even for some small molecules you may not see them. So we have another technique, a softer ionization technique called chemical ionization that we can use.

So in chemical lionization, what we do is we take a guess and we flood the ion source with a gas. I'm going to choose methane for this. Methane is often use. And we ionize that methane.

And then the ionized methane reacts with more methane to produce a super acid, CH5 plus, and a methyl radical. Now, your molecule goes in and it encounters the CH5 plus. What do you think happens to it?

**AUDIENCE:** It's acidified?

**JOHN DOLHUN:** Yeah, it's going to get acidified. It's going to get protonated. So this CH5 plus protonates your molecule, and you get this huge M plus 1 peak.

So this is great. If we have these big proteins and peptides and we want to know what the molecular weight is, we can use chemical lionization, put them in there, and we'll see the big M plus 1. We won't see a lot of fragmentation, but at least we can get some molecular weight information out of the system.

CH5 plus is an interesting molecule. You all know from your chemical principles that CH4 is SP3 hybridized. So when those two methane molecules collide and it throws the hydrogen in, that hydrogen pushes another hydrogen out of the way and it forms a three-centered, two-electron bond.

This is a pentavalent carbon atom with a positive charge. That's a carbocation. That's the definition of a carbocation in chemistry.

This is also called the methanium ion. And this is one of the last unsolved problems in physics, because no one can isolate this stuff. It's very difficult to isolate.

And about three years ago, at the University of Cologne, they actually trap some of this stuff in an ion chamber at very low temperatures, near absolute zero, and they studied the vibrational spectra. What they saw was all these hydrogens are coming off, moving around the carbon atom. They're breaking off and moving around. So now, scientists are wondering whether this thing actually has any structure at all.

So that's chemical ionization. Sometimes, electron impact and chemical lionization, both of them won't work for us. We may have a molecule that's too big or that's too nonvolatile. So we go to fast atom bombardment, electrospray, or matrix-assisted laser desorption spectroscopy.

Fast atom bombardment is pretty simple. You take your sample, mix it with a little bit of glycerol, put it on a metal target, and then we shoot xenon and argon atoms at it, very high speed, high energy. And the glycerol in your sample absorbs the shock of the impact with those atoms.

And we have some trifluoroacetic acid in there, TFA, so that we can produce these M plus 1 peaks. The advantages of fast atom bombardment are for high molecular weight samples, nonvolatile compounds, EICI don't work. Molecular weights here, I've seen 20,000 or so.

So you can go out-- they're constantly making innovations with these. The next technique, electrospray ionization, is quite interesting. The ions are produced, the molecule is ionized, and it's done at a very low pH. And there's a nebulizer that actually shoots out like an aerosol through a high voltage and you get these charged droplets coming out, very large droplets with a lot of positive charges on them.

And then we can take a stream of warm nitrogen gas and evaporate those down and you get a smaller droplet and then that disintegrates. And what you end up with are these multi-protonated molecular ion peaks. You could have an M plus 20. You could have 20 hydrogens on there, or 10 hydrogens, or you get a variety of numbers.

And what that does is it expands the mass range. Let's say, for example, you have a molecule that maybe weighs 70,000, and you produce a-- you produce an M plus 20. So what you have to do is-- you're going to have a molecule like that.

You're going to have to divide, now, by the charge to get where this molecule is going to show up. Because it's mass to charge ratio, and if the charge is 20, if you divide this out, you're going to get something around 3,501. That's where the peak is going to show up in your spectrum. So the advantage of this technique is you can take molecules that are 70,000, 80,000, and your peaks could come out at 3,500 or much less. So it expands the whole mass range of using a mass spectrometer.

The last technique is MALDI, Matrix-Assisted Laser Desorption Ionization, and we would use that principally for solids. And these would be like the big carbohydrates, the big peptides and proteins. And you take your crystal and you dissolve it in a matrix, a solvent, and you put a chromophore in to absorb the laser light, and then this sample begins to evaporate and you get beautiful crystals on this metal target. And then you shoot a nitrogen laser at it, 337 nanometers, and you end up getting M plus H speaks out.

So you can take these large solids. And molecular weights here can go out quite a bit. So the advantages of all these techniques are they can help us with nonvolatile, high molecular weight samples and getting spectra.

We've already talked about the inductively coupled plasma in one of the lectures, so I'm not going to talk about that. But I would like to cover a couple types of instruments that you will experience. The first is the magnetic sector. The last is the one we have in the undergraduate lab, the radio frequency quadrupole filter trap.

So let's start with the magnetic sector. You'll see some similarities to these. So here is your ion source. You can see the filament here. And the filament is shooting out an electron beam at your sample.

It's about 70 electron volts. That's like about 1,600 kcals of energy. And 100 kcals, you can break a bond. So with all that energy slamming into your molecule, it not only ionizers the molecule, it starts to break apart into fragments. And the fragments in this magnetic sector instrument get ushered through a pair of focal plates and then they get sent into the mass analyzer.

There's an electric field perpendicular to a magnetic field. The electric field controls the velocity of the ions, and the magnetic field will cause the deflection with the heavier ions deflected less than the lighter ions. So you kind of get a spectrum here on the detecting screen based on how they're deflected by the magnet.

Time of flight, this is actually one of my favorites. There are a couple advantages to this. One is it has almost an unlimited mass range. The second advantage is you can do very small amounts of sample with this.

So what happens in time of flight is your samples get ionized in the ion source here. They get ionized similar to all the other mass spectrometers. But then they get shot out into a flight tube and they get shot out at the same kinetic energy, all the ions that are going in there. And kinetic energy is equal to 1/2MV squared, which is also proportional to the charge times the voltage when they're being shot out.

So if you look at the kinetic energy, you can see that the velocity is square root of 2 of the kinetic energy divided by the mass. So that means that the heavy ions are kind of lagging here. They're traveling slower because they're heavier.

So when they're in this tube, they actually measure the time of flight through the tube. That's what this-- it's called time of flight, right? So the time of flight is the distance divided by the velocity.

Now, if you put that back into this equation and you solve it out, you'll see that the mass to charge ratio is equal to the square of the time of flight divided by the distance. This is a great salute to the engineers. They designed this system.

This machine is so simple. There's no electric field. There's no magnetic field. All there is is a tube.

Doesn't this remind you of TLC with the spots? Except there's no mobile phase and no stationary phase here, right? So this is a great instrument. And that's how your mass spectrum is determined.

Now, the next one, which is also kind of like the Cadillac of all mass spectrometers, is the Fourier-transform ion cyclotron resonance instrument. This instrument, ions are generated the same way as in the other mass spectrometers, but when they're generated, they start to get pumped to different pumping stations, and every pumping station has a higher and higher vacuum. So the pressures continue to drop until the ions reach this box, and then everything breaks loose here.

Because in this box, you've got a temperature of about 2 Kelvin. You've got a magnetic field of about 21 tesla, and there's an electric field in there. And if you think about this, you have a charged particle traveling at a certain velocity and it enters-- it enters the magnetic field. What happens to it? What's going to happen to that charged particle when it gets into that magnetic field? Autumn?

**AUDIENCE:** It'll go around.

**JOHN DOLHUN:** It's going to start to spin, yeah, like a cyclotron. It's going to be-- it's going to be spinning like this. In fact, when the particle goes in there-- let me give you an example, like 100 molecular weight fragment, 100 Dalton could travel 30 meters in about one second inside of that box just crazy. So it has a centripetal force on it. And force is mass times acceleration, right? So mass times acceleration.

So this is our system. And the angular velocity of that particle is given by velocity over r. So if you plug that in here, the cyclotron frequency of that particle, that velocity is nothing to do with its velocity. It's only to do with mass and charge. That's the bottom line. That's incredible.

And if we hold the magnetic field constant, then the cyclotron frequency is the mass to charge ratio of that particle. So what comes out of this is convoluted signals like this FID, these sine waves, and we do a Fourier-transform on that signal and pull out the mass spectrum that we want. So it's quite interesting.

It's the most sensitive method of ion detection in the world. The resolution is greater than 10 to the 7 on this instrument. And if you think about it, that spinning particle, it's spinning so many times, the detector is on the outside here.

The difference between this and all other forms of mass spec is the detector is on the outside, so it doesn't-- the ions never reach the detector. They only record the image current from the ions as they're going by. And it's recording it over and over and over again. That's why you've got such beautiful resolution here.

And then you've got the system we're going to use, the quadrupole filter radio frequency system. So what we have for our mass analyzer is four rods in parallel, and the opposite rods are electrically connected. There's a DC voltage put on those rods. And then an RF voltage is superimposed on one pair of rods over the other.

And it's the voltage of that pulsed radio frequency field and the frequency that determines which ions get through these rods. Only one ion can actually make it through the rods at a time, depending on the frequency of that radio frequency pulse and the ratio of voltages on those rods. And the other ions basically just crash into the sides here.

So a couple of things, before you actually come in the lab and do the lab, we have to actually tune the mass spectrometer up. Because mass spectrometers have an internal mass scale. Can actually go off kilter. And so we've got to make sure that every mass is where it's supposed to be.

The detector gain has to be cranked up so that we can see peaks far enough out. To do that, we use this compound, perfluorotributylamine. This is the stuff that we actually have in the mass spectrometer in a little vessel, and when we do the tune, the vessel opens up, and a whiff of this comes out.

And the beauty of this is it can fragment down here. ScF3 can fall off. You get a 69 peak. Can do that from three directions.

You can lose one of these polyfluorinated butyl groups from either of three directions and you get a 219 peak, or you can clip it right here and you get a 502 peak. And that's pretty much all you see. You see the 69, the 219, and the 502. The spectrum is very simple. And the molecular weight is 502. So

We key in on these and adjust the internal mass scale of the instrument and make sure it can separate peaks 1 AMU apart. And for your samples, your samples will be under molecular weight of 200. So if we can go out to 500 and have it tuned up, we'll be fine.

This is water. Very simple molecule. This is your chance to talk. I want you to-- we're going to actually look at this. What I'd like to do is I'd like to see what the mass spectrum of water looks like. So we're going to ionize some water.

And we've got our abundance here and our mass-to-charge ratio. So what would you see in the mass spectrum of water? Which peaks would you see? Royce? Oh, you were scratching yourself. Yeah. [CHUCKLES] What would you see? Yes, Alec?

**AUDIENCE:** M-to-C equals 18.

**JOHN DOLHUN:** 18, yes. You'd definitely see an 18 peak. That's your ionized water molecule. What else? Alec? There's not much to fragment, is there? Well, what would you get if you tore this apart?

**AUDIENCE:** You'd get a 1.

**JOHN DOLHUN:** A 1, yes, you'd definitely see a 1 here. That's your hydrogen. What else? Yeah.

**AUDIENCE:** You might see a 16.

**JOHN DOLHUN:** Yep, you'd see a 16. What else?

**AUDIENCE:** Will you see a 17?

**JOHN DOLHUN:** Yes, you would. Very good. And that is-- that's the whole spectrum of water, four peaks. Yes, Autumn.

**AUDIENCE:** Could you get 32 or 2 in the oxygen and hydrogen diagrams?

**JOHN DOLHUN:** You could get-- if you're looking at air, air has diatomic gases in it. So if you put air in, you would see some of those peaks, yeah.

Yeah, let's look at air, since you mentioned that. Let me just put this down here. I mean, air has diatomic gases. So what would you see in air? Yeah, Noah.

**AUDIENCE:** A 28.

**JOHN DOLHUN:** A 28, good. So you'd see a 28 here. Yep, what else?

**AUDIENCE:** 32.

**JOHN DOLHUN:** Yep, you'd see a 32.

**AUDIENCE:** 44.

**JOHN DOLHUN:** Very good. Good old carbon dioxide. Yep. What else?

**AUDIENCE:** 18.

**JOHN DOLHUN:** Yeah, you'd see water. We hate water, but it's in the air, right? So you definitely, definitely would see an 18 peak. What else? How about some of the noble gases? They're in the air. Which one?

**AUDIENCE:** Ne.

**JOHN DOLHUN:** Neon, yeah. Neon is 20. Any others?

**AUDIENCE:** Would you see argon?

**JOHN DOLHUN:** Yes, argon. Argon is 40. What other gas? Yes.

**AUDIENCE:** Would you see helium or not?

**JOHN DOLHUN:** Very little. Very little. What else? What's a couple of the other big inert gases?

**AUDIENCE:** Xenon?

**JOHN DOLHUN:** Xenon, yes, 131. What about the Superman gas?

**AUDIENCE:** Oh, krypton.

**JOHN DOLHUN:** Krypton, yes. 84, krypton. And you may see a 29 peak, because you might see nitrogen-15, nitrogen-14. Because the mass spec will detect isotopes. You also, for oxygen, you could see a 34 peak, because you've got-- you might have some oxygen-18, oxygen-16.

But you've hit them. And these just came out-- this was I think in not*Time* magazine, but one of the-- one of the magazines came out with the periodic table. The whole issue was on the periodic table. And they listed all the gases that are in the air. So it's kind of neat.

So let's move on here. I want to show you what a mass spectrum looks like. This is hexane, your good old friend, right? C6H14. So what you've got here is you've got your molecular ion peak at 86, right? And then everything to the left of that is fragments breaking-- the molecule breaking apart.

And notice the intensity of the peaks. One of the peaks is a base peak. That means the detector counted that more than any other peak. So what the detector does is gives that 100 and all the other peaks are relative to that base peak. And when we give you your mass spectrum, we'll give you a sheet with the abundances on it.

Notice, if you take this base peak, 57, and you subtract it from 86, that's a loss of 29, isn't it? So it's pretty much just an ethyl radical falling off, and you've got this butyl cation. The butyl group has the plus charge. That's your 57 peak. It's that simple.

So you take your peak, subtract from the molecular ion, see what's been thrown off. What about the m plus 1 peak here? What is that? There's no chemical ionization going on here. [CHUCKLES] What's the m plus 1 peak? Yes, Deb.

**AUDIENCE:** [INAUDIBLE]

**JOHN DOLHUN:** Did you say something with carbon?

**AUDIENCE:** Yeah, 13.

**JOHN DOLHUN:** Carbon-13, very good. Yeah, carbon-13. So carbon-13 has an abundance of 1.1%. 1.1% of all carbon is carbon-13. Look up here. You got six carbons, right? So 6 times that-- 6.6% of the carbons are carbon-13.

So if I take this molecular ion peak, which is-- my eye is saying it's about 15% abundance, if I multiply that by 0.066, I get 1%, that m plus 1 peak. That's approximately what we're talking about.

What if we didn't know the number of carbons? We didn't know the structure? We could work backwards and figure it out from the molecular ion abundance and the m plus 1 abundance.

The number of carbons would be equal to the abundance of the m plus 1 divided by the abundance of the m plus dot times 100 divided by 1.1. That would give you the number of carbons in your molecule.

So mass spec can not only determine the molecular weight, you can determine the molecular formula of your system. You can also determine the number of isotopes and elements that are present in your system.

So there are other isotopes. Look at chlorine-35 and chlorine-37 here. If you see this in the molecular ion region of your spectrum, and your molecular ion is separated by 2 mass units, it's a dead giveaway. That's chlorine's signature. That means you have a chlorine in your molecule.

Bromine is even simpler. Bromine has two peaks, both equal abundance-- the 79 and the 81 separated by 2 mass units. Here's an example.

So here's a mass spectrum. Look at our molecular ion region here, separated by 2 mass units, ratio of 3 to 1. What do we have?

**AUDIENCE:** Chlorine.

**JOHN DOLHUN:** A chlorine, yes. OK? So if you take this-- take this peak here, this is 77, subtract 112, you have a loss of 35. So if you take the-- if you simply take the two things and put them together, the 77 is the phenyl ion. So if you just stick a chlorine on there, you got chlorobenzene. That's the spectrum.

Here's another spectrum. This is very interesting, because all these peaks are separated by methylene units, 14 mass units, CH2 units, all through the whole spectrum. When you see that, you know you've got a long chain of carbon atoms as part of your spectrum.

So this particular spectrum is decane. And it ionizes at all these different bonds, producing this spectrum with this logical lost ion series. There's another one, dodecanoic acid, which has all these methylene units, which is a dead giveaway for a long chain of carbons connected to something.

Here is a simple spectrum. This is 2-propanol. Now, the molecular weight of this is 60. But look down here. Do you see 60? There's no molecular ion there. So this molecule is doing something that's energetically very favorable to itself to produce a 59 peak. What do you think it's doing? It's one less than the molecular ion, right? Yeah.

**AUDIENCE:** It's losing the H on the OH.

**JOHN DOLHUN:** Yes?

**AUDIENCE:** It's losing the H on the OH.

**JOHN DOLHUN:** Yes, Hannah. Loses the H, right. So if you take-- this guy ionizes here. And it has resonance, because you can throw that positive charge out onto the oxygen. So it's really, really a very stable system. It loves to do that.

And look at the base peak in this spectrum, 45. You can lose a methyl group from either side here, and you've got a 45. It's left over. And it's resonance-stabilized, because the positive charge can resonate with this oxygen here.

So that's the idea. When you see a base peak, you know the molecule is loving to do something that's very favorable. And in this case, it could cleave from two sides.

So this is an ester. This is ethyl-isobutyrate. I don't know if this is one that's been given out. I'm not talking. But this is a simple spectrum. And the idea here is, what you do is you're going to take this, and you're going to break it apart to try to figure out where those peaks are coming from.

So if you cleave the ester here, right, right by this carbonyl, you lose this-- do this alpha cleavage, you'll get this 71 fragment, which can then lose carbon monoxide to give you a 43 fragment. So if we actually go back here, there's our 71, and there's our 43.

And then, look at this right here. You can actually lose a neutral molecule of ethylene. Transfer the hydrogen back to this point. And you're losing CH2-CH2. That's an example where one piece of the molecule retains both the plus charge and radical that I talked about.

And here's your fragment, your 88. There it is there. So the idea is to go through here and try to take your ester and try to break it up and substantiate some of the fragments from-- in a table or something, to show that what you've got. And that way-- that way you'll convincingly convince someone that you-- indeed that is your product.

Do you have some questions about this? So if you're on day four, you'll be doing the mass spectra today. And I guess you turn in your guesses for your unknowns today, right? Good.

It was easy, right? Yes. It was too easy, wasn't it?

**AUDIENCE:** Nah.

[CHUCKLING]