

CHEMICAL HERITAGE FOUNDATION

NICO M. NIBBERING

Transcript of an Interview
Conducted by

Michael A. Grayson

at

Home of Michael Gross
St. Louis Park, Minnesota

on

7 and 8 June 2013

(With Subsequent Corrections and Additions)



NICO M. NIBBERING

ACKNOWLEDGMENT

This oral history is one in a series initiated by the Chemical Heritage Foundation on behalf of the American Society for Mass Spectrometry. The series documents the personal perspectives of individuals related to the advancement of mass spectrometric instrumentation, and records the human dimensions of the growth of mass spectrometry in academic, industrial, and governmental laboratories during the twentieth century.

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NICO M. NIBBERING

1938 Born in Zaandam, Netherlands on 29 May

Education

1960 Kandidaatsexamen, Chemistry, University of Amsterdam
1964 Doctoraalexamen, Chemistry, University of Amsterdam
1968 PhD, Chemistry, University of Amsterdam

Professional Experience

University of Amsterdam, Amsterdam, Netherlands
1967-1975 Permanent staff member in charge of mass spectrometry
1975-1988 Associate Professor of Organic Mass Spectrometry
1980-1988 Full Professor of Organic Mass Spectrometry
1988-2000 Scientific Director of the Institute of Mass Spectrometry
1988-2001 Full Professor of Chemical Mass Spectrometry

Honors

1964 Unilever Chemistry Prize
1968 Shell Research Chemistry Prize
1991 International Mass Spectrometry Thomson Medal
1992 Johannes Marcus Marci Award

ABSTRACT

Nico M. Nibbering was born in Zaandam, the Netherlands, one of eight children. . When school resumed after World War II, Nibbering did well and tested into high school, where he chose the science and mathematics track and where his physics and chemistry teachers influenced him to attend college. He entered the University of Amsterdam and majored in chemistry under Thymen de Boer. Nibbering also obtained his master's and PhD degrees there and became head of the mass spectrometry department.

Nibbering toured the United States, meeting a number of prominent scientists and learning more about mass spectrometers. He was especially interested in a drift cell ion cyclotron, and on his return to the Netherlands he persuaded de Boer to purchase a Varian Syrotron. This was only the first of his many instruments, as different types of spectrometers were needed for different types of problems. He refined his interest in gas phase ion chemistry during a few months spent in Fred McLafferty's lab at Cornell University and became entranced with a Fourier transform (FT) instrument. Back at home he and James Dawson transformed a drift cell ion machine into an FT spectrometer in just a year. When he considered leaving for Utrecht University, the University of Amsterdam established a research institute for him.

Throughout his interview Nibbering talks about his work and the variety of mass spectrometric problems and solutions. He gives examples of his many different kinds of spectrometers and their homemade modifications. He emphasizes the importance of his travel and his networking with other scientists around the world, calling his initial trip to the United States a highlight of his career. He discusses financing his expensive instruments and the research institute established for him. He gives credit to his many colleagues and collaborators. He believes that the most important of his very many publications is his master's thesis and that his important contributions have been in gas-phase ion chemistry study. He advises would-be scientists to do what they love and to do their best; enthusiasm is crucial. He says that there are three ingredients in mass spectrometry: fundamental research; development of new ideas and methods; and applications. Nibbering details some of the more important developments in mass spectrometry, especially its use in medical science. He thinks the future of the field includes smaller, easier-to-use instruments with more and almost universal applications.

Nibbering is retired, but his fascination with mass spectrometry continues undiminished. He is a member of the Royal Netherlands Academy of Arts and Sciences, and he is still editor of the *Wiley-Interscience Series on Mass Spectrometry*.

INTERVIEWER

Michael A. Grayson is a member of the Mass Spectrometry Research Resource at Washington University in St. Louis. He received his BS degree in physics from St. Louis University in 1963 and his MS in physics from the University of Missouri at Rolla in 1965. He is the author of over 45 papers in the scientific literature. Before joining the Research Resource, he was a staff scientist at McDonnell Douglas Research Laboratory. While completing his undergraduate and graduate education, he worked at Monsanto Company in St. Louis, where he learned the art and science of mass spectrometry. Grayson is a member of the American Society for Mass Spectrometry (ASMS), and has served many different positions within that organization. He has served on the Board of Trustees of CHF and is currently a member of CHF's Heritage Council. He currently pursues his interest in the history of mass spectrometry by recording oral histories, assisting in the collection of papers, and researching the early history of the field.

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instrument paid for by University of Twente. More travel and international papers. Pyrolysis. Importance of cleanliness in instruments. Patents. Bernhard Linden and liquid injection field desorption (LIFDI).

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Single most important publication his master's thesis; formation of phenol. Other highlights: trip to United States; building FT in one year and one day. Technical explanations of his work. Veronica Bierbaum, editor of Festschrift for Armentrout's sixty-fifth birthday, collaborated on exploration of Hund's rule regarding notch ejection technique on the FT. Major contributions in gas-phase ion study, especially mechanisms. More about colleagues and students from his lab, and where they are now. Interest in motorcycles. Using his instruments for both analysis and research. Editing *Mass Spectrometry Review*; also *Wiley-Interscience Series on Mass Spectrometry*. Organizing and financing international conferences. More about other colleagues. Advice: do what you like and do your best. Enthusiasm crucial. Mentoring. Competition. Women in science. Important changes in mass spectrometry include especially medical science. Future includes smaller, easier-to-use instruments with more applications.

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INTERVIEWEE: Nico M. Nibbering

INTERVIEWER: Michael A. Grayson

LOCATION: Home of Michael Gross
St. Louis Park, Minnesota

DATE: 7 June 2013

GRAYSON: Today is the seventh of June, 2013. We are at the home of a colleague, Michael [L.] Gross, in St. Louis Park, Minnesota. I'm starting the first part of an interview of a scientist by the name of Nico Nibbering, and we're going to spend some time talking about his career in science in general and mass spectrometry in particular. And so, with that much of an introduction, I'd just like to go ahead and start with how—the very early part of your life, your family, and particularly their interests or their attitude towards education and intellectual pursuit in general. So, you were born in probably what, nineteen . . .

NIBBERING: Twenty-nine of May 1938. In Zaandam, [Netherlands].

GRAYSON: [. . .] Very good and that is in which country?

NIBBERING: It is in the Netherlands. It is about fifteen kilometers north from Amsterdam, [Netherlands].

GRAYSON: Ah-ha. And your parents, what did they do for a living?

NIBBERING: My father was a factory man, and my mother, before she married, she made clerical garbs, I think.

GRAYSON: This could be for people that were in a religious . . .

NIBBERING: For the Roman Catholic Church.

GRAYSON: Very good. Can we have the names of those people?

NIBBERING: Yes, the name of my mother is Hendrika Clynk.

GRAYSON: The last name was?

NIBBERING: Clynk [. . .]. A strange name in the Netherlands. Because it is possibly Scottish in origin. But that depends on how much I can say about that because we didn't figure it out—where we came from—there was a family who did it. And that went back until somewhere in the thirteen hundreds, and they found that we were descendants from the Sinclairs in Caithness in Scotland. And the man was Earl of Caithness and the Orkney Islands.¹

GRAYSON: [. . .] Okay, very interesting, so there's this . . .

NIBBERING: [Yes], it's a long, long way ago, and they had a castle, of course, there at that time. As I said he was the Earl of Caithness and there is the Gulf of Sinclair [Sinclair's Bay].

GRAYSON: Glove?

NIBBERING: The Gulf of Sinclair.

GRAYSON: Gulf?

NIBBERING: [Yes], Gulf of Sinclair, and that is called the bay area. And that—Sinclair, that sound, then that is somewhere connected with the name Clynk in the end. But the black sheep of that family became ship surgeon and he ended up—well his later-born children, let's say that, I don't know—but in France. And then with the Huguenots, they came to the Netherlands, so my grandfather, his name was Clynk also. The way he pronounces it is Clynk. And it was in the south of the Netherlands and therefore the name of my mother is then Hendrika Clynk.

GRAYSON: Oh my, okay.

¹ William Sinclair (1410–1484) was the first Earl of Caithness, third Earl of Orkney, and Baron of Roslin.

NIBBERING: I don't know many other forenames. I mean, this was her first name and then the family name.

GRAYSON: And then your father?

NIBBERING: My father was Dirk Nibbering. [. . .] I don't know whether he had more forenames but that is at least known. And he was born in De Rijp, [Netherlands].

GRAYSON: [. . .] Okay.

NIBBERING: [Yes], De Rijp, in North Holland.

GRAYSON: That's in . . . ?

NIBBERING: Like Zaandam, North Holland is the province in the Netherlands.

GRAYSON: Okay, North Holland.

NIBBERING: That also holds for Zaandam.

GRAYSON: [. . .] And so what was their educational background?

NIBBERING: My father had only elementary school. And I think my mother had at least an elementary school and then perhaps a school where you learned about household managing. Well, to repair clothes and these kinds of things. It was a lower based education following the elementary school. I can say, of course, to you, Mike, there was nobody in our family who had studied before and had an academic career, et cetera.

GRAYSON: Okay.

NIBBERING: And I must also say that I was born in 1938. So in 1940 the Second World War started. During that time, during the Second World War, I went to school in 1944 to the

elementary school, but it was a very hard and cold winter, so you could not immediately start the term at school because the school didn't work.

GRAYSON: Didn't have any heat?

NIBBERING: That was one of the problems of course. And I also must say then that why I wanted to learn or . . . eager to learn things I asked my father to buy a book on simple mathematics that you learned at the school and Dutch language. And my mother, she had the capability to explain to me. So I learned from her to do some mathematics in Dutch language in the time that I didn't go to school.

GRAYSON: Okay. So this was like when you were probably . . .

NIBBERING: Six years.

GRAYSON: Six years old?

NIBBERING: Six years old, yes.

GRAYSON: Okay. So it was a little bit like almost what we call homeschooling here in the United [States of America].

NIBBERING: Homeschooling because, at that time, it was difficult to get to school. That changed, of course, in May 1945 because springtime, then you could go to school. And then, in the first class of the elementary school I remember that the teacher, she was a lady, suddenly on the fifth of May she did see a Dutch flag over the River Zaan. Of course, Zaandam, hey? There is a stream called the Zaan.

GRAYSON: Okay, so the Zaandam refers to like a dam at the Zaan River?

NIBBERING: [Yes], Zaan River.

GRAYSON: So over the river . . . ?

NIBBERING: [Yes], there she did see suddenly the Dutch flag. That meant that we were free, liberated.

GRAYSON: Oh, oh, okay.

NIBBERING: And that I remember very well as a child.

GRAYSON: So prior to that time, you were under what governmental jurisdiction before the Dutch were liberated?

NIBBERING: Europe . . . we were occupied by the Germans.

GRAYSON: This was up until 1945?

NIBBERING: 'Forty-five. The fifth of May, that was the liberation.

GRAYSON: Okay.

NIBBERING: The occupation by Germans was then over. I remember also, as a child, at the school square, the bombers coming over—the [Avro] Lancasters, They came over the school very low. You could almost see the pilot and the man who was shooting. But what I also must say, I am the oldest one of a family of eight children.

GRAYSON: Okay.

NIBBERING: What was now the problem—I think the family had too many children so my mother, although she could teach me, she was very inert in some way. And my father was a very nervous person. He always went out to get food. That was difficult at that time because you had to go on a bicycle. But there were of course many problems to keep the bicycle running. And then to go through the country, <T: 10 min> where there were always Germans, to pick up food from farmers. And so in that way we got food. But I remember that after the war was over I had to go to the south of the Netherlands to a convent with nuns to get, again, in good shape because I was not in good shape because of malnutrition.

GRAYSON: Okay. This would have been 1945?

NIBBERING: 'Forty-five. [. . .] And then, what I did, as the oldest child I tried, in the morning, to make the food for the brothers and sisters. I don't understand why my mother was so inert. Then when they were fed, then I started to clean up, and then I started to do learning about mathematics and language. And don't ask me why—I mean, why that I did.

GRAYSON: So then you were pretty young, too, at that time?

NIBBERING: [Yes]. But then my father took me, at the end of '45, so in December, to his sister. So my aunt and my uncle. They lived in another section of Zaandam, called 't Kalf. I don't know whether that is important for the interview.

GRAYSON: Well let's get the name, spelling, down. [. . .]

NIBBERING: I had the holidays. My father took me on his bike to the aunt and uncle, and then two weeks later he came back and he asked me whether I wanted to stay there. And then I said yes.

GRAYSON: [laughter] They had no children, your . . .

NIBBERING: They had five children.

GRAYSON: Oh, okay.

NIBBERING: But, I said yes, and later on, of course, I thought, "Why did I say yes?" And I discussed it also with Michael [Gross], of course we know a lot from each other. I think that at my own parents' [household] it was not organized. I tried to organize. And it had to do, of course, with the circumstances of the war, et cetera, you can understand.

GRAYSON: [Yes].

NIBBERING: And now I came into a family where it was organized. Therefore I might have

said unconsciously, “Yes, I would like to stay here.” And then I grew up there. So I am the only one, of all the brothers and sisters, who grew up in a normal family because the sisters went to—how do you call it—a convent run by nuns and the brothers went to institutions run by brothers.

GRAYSON: Oh wow, okay.

NIBBERING: And that’s another thing. The parents . . . it was for the children’s protection organization, they took care of these children from families where the parents could not do it. So the parents were not allowed anymore to raise their kids.

GRAYSON: Okay.

NIBBERING: I hope that it’s clear—protection?

GRAYSON: It’s like the family was just not functioning well enough to get . . .

NIBBERING: But not in a way that the parents were nasty, or said, well, we don’t take care of them, but they could not.

GRAYSON: [Yes], they didn’t have the resources, the money.

NIBBERING: They didn’t have the resources, and the circumstances Because I now would—just, perhaps, to write it down: my father had, always, problems that that has happened, because he always said, “But my children have a good position in life.” [Yes]? So that was saying to himself, “That happened, but fortunately it went okay.” [laughter]

GRAYSON: So what about your other brothers and sisters? They went, obviously, in different ways.

NIBBERING: [Yes].

GRAYSON: So they all were raised okay and they were . . . they had . . .

NIBBERING: Now one of them, he became a sailor man and he was allowed to go, when he was seventeen years old, on the Holland America Line ship company. That was exceptional, because most of the time these children were held in these institutions. But he had a very good influence on the other children, so they allowed him to go on to make trips with the Holland America Line. Later on, he ended up to be an engineer in a tugboat, et cetera.

Then two sisters were twin sisters [of] each other. They did go to school and then they married. Also the youngest one so elementary school and then married. I had a very good brother, Henk, but he passed away because of a brain infarct. That is, of course, a problem. Oh, and one sister is living in Sardinia in Italy because she married an Italian person. And then I have a brother in Canada, in Alberta. We write him but we never get an answer. That can also happen.

GRAYSON: I was just in Canada a couple of weeks ago interviewing Paul Kebarle.²

NIBBERING: Oh [yes].

GRAYSON: So that was pretty interesting. It was fun. Basically your aunt and uncle were probably the strongest influence, then, from age six or so on.

NIBBERING: Yes, seven . . . from seven, yes. That background was they also went only to elementary school. So Aunt Neel, *tante* Neel in Dutch. The full name, the official name, is Petronella. [. . .] Nickname, Neel. And we had Uncle Piet. [. . .] And the family name was Piet Konijn. Konijn. [. . .] *Konijn* is “rabbit.”

GRAYSON: Rabbit?

NIBBERING: [Yes], *konijn*.

GRAYSON: Ah, okay.

NIBBERING: And he was also a factory man. Also he owned animals like goats, and pigs, and

² Paul Kebarle, interview by Michael A. Grayson at University of Alberta, Edmonton, Canada, 22 May 2013 (Philadelphia: Chemical Heritage Foundation).

all these kinds of things. And the aunt—both my father [and] his sisters and brothers, they became very young orphans. And so Aunt Neel . . . she worked, also, with a farmer, but my father had, also, to work with a farmer because that was the way in which that happened with each other. And in some way he hated farmers, and I think he had a very bad childhood with farmers. Okay, that is not so important.

But the thing was, I went to the elementary school in 't Kalf, that section, and the headmaster of that school, he did see that I did very well in some way. And the headmaster came to my aunt and uncle to discuss whether I could go to high school, because that was his idea. [Fig. 1] Both the uncle and aunt—nobody went to such a school. So when I heard that it is named *Hogere Burgerschool* [HBS]—Higher Citizens' School, you understand, if translated—I heard that, sitting in the room, and as a child I thought, “But I don't belong to the higher citizens. I came from a very simple family.” *HBS*, or high school, that was, for the aunt and uncle, another world. Well, he was an authority at these times . . . headmaster of a school was of course an authority in the eyes of my uncle and aunt. [. . .] And that was a part of Zaanlands Lyceum.



Figure 1. Nico Nibbering as a student

GRAYSON: Okay, what's that about?

NIBBERING: Zaanlands Lyceum, so it has a division of . . . if I say *Hogere Burgerschool*, <T: 20 min> we call it HBS, of course. HBS, and it was part of at Zaanlands Lyceum. [. . .] I had to do an examination to enter that school.

GRAYSON: This was after you completed eighth grade.

NIBBERING: The elementary school.

GRAYSON: Elementary school.

NIBBERING: And I passed that examination, I was okay. So in that way I came to high school.

GRAYSON: Now this headmaster, he obviously recognized talent.

NIBBERING: [Yes].

GRAYSON: Do you remember his name?

NIBBERING: [Yes], Van Oerle.

GRAYSON: [. . .] So he was instrumental in recognizing the . . .

NIBBERING: Very instrumental.

GRAYSON: Okay.

NIBBERING: Very instrumental.

GRAYSON: Do you know if he did this for other students?

NIBBERING: [Yes].

GRAYSON: Okay. So he, kind of, was picking up . . .

NIBBERING: There were more from 't Kalf who went to high school.

GRAYSON: So that was his job was to make sure that the . . .

NIBBERING: That was also—how do you call it—the strict headmaster of course. You know how that works.

GRAYSON: [laughter]

NIBBERING: But, now, he took care of these—he looked [at] which students, or children, could do it and then he took action. That was very good, so it's instrumental. As you say, he has been instrumental.

GRAYSON: Very good. So did you go to a particular high school, Higher Citizens' School, or was there just one that everybody went to at that time?

NIBBERING: No, it's—Zaanlands Lyceum was well-known for the region of Zaandam. And then of course you start in the first year, the first class, and then after half a year then, a *rector*—we have a *rector* and *conrector*. [. . .] The *conrector* was responsible for the *gymnasium* division. Now see, Mike, Zaanlands Lyceum, the HBS, and the *gymnasium*.

GRAYSON: Oh, right.

NIBBERING: And the *conrector*, he asked my aunt and uncle, including myself, to come over to discuss the following. He wanted [me to] participate in the program to see whether I could do *gymnasium*. You know, the aunt and uncle, what did they say if the *conrector* is saying that this? [Yes]. And I was eager to learn in some way. I thought it was a nice idea, so therefore I participated. And then I ended up in the second class, that I really went over to the *gymnasium*. *Conrector* DeVreese was the name, *Conrector*. [. . .] And he was a specialist in Indo-Germanic languages.

GRAYSON: Okay.

NIBBERING: Thirteen of them, he managed to But he gave, also, art and history from the Middle East. He taught Latin and Greek of course. That was no problem. I must say, in '54—that is, also, I remember very well about religion. He pointed out [that] Jerusalem [Israel] was a difficult place that we might expect to get problems, because there were the Islam, Judaism, and Christianity. And as a child—he had very interesting stories . . .

GRAYSON: Oh, [yes].

NIBBERING: And that he told it—in some way, perhaps, he indicated problems. We had had the Second World War . . . perhaps that has also a reason unconsciously in your mind.

GRAYSON: So he kind of foresaw that that portion of the Middle East was going to be . . .
<T: 25 min>

NIBBERING: And difficult. Not war, but a difficult situation there. And that is nowadays true, I think, huh?

GRAYSON: Oh, [yes].

NIBBERING: [laughter] But then, if you have been four years on the *gymnasium*—so you've got Latin, Greek, history, English, German, French, mathematics, chemistry, you name it. Then after four years you could make a choice whether you take the alpha direction—that means the old languages, Latin, Greek, as main part.

GRAYSON: Okay.

NIBBERING: Or you took the science part. So I took . . . so, alpha is the direction, languages.

GRAYSON: Alpha as in Greek alpha?

NIBBERING: Alpha. Greek alpha.

GRAYSON: Okay.

NIBBERING: The *gymnasium*-alpha or *gymnasium*-beta.

GRAYSON: Oh, beta.

NIBBERING: Beta. Beta was the science part. You've still got Greek and Latin but less than at the alpha.

GRAYSON: So alpha was like liberal arts or . . .

NIBBERING: Or philosophy, for example.

GRAYSON: [Yes].

NIBBERING: You had to translate Homer. We read Caesar . . .

GRAYSON: The classical education.

NIBBERING: Classical. Classical education, yes.

GRAYSON: So you chose the beta?

NIBBERING: Then I was at an age that I decided myself to take beta.

GRAYSON: Okay, so this was probably about . . . you were at this time maybe . . .

NIBBERING: 'Fifty-four.

GRAYSON: So eighteen, or sixteen?

NIBBERING: In '56 I was eighteen. So I was sixteen, then, at that time that I decided that.

GRAYSON: Okay, and so I noticed that even in the *gymnasium* you had quite a bit of language exposure in modern languages?

NIBBERING: [Yes].

GRAYSON: So you grew up in Amsterdam?

NIBBERING: In Zaandam, [yes].

GRAYSON: What was your native language as a child?

NIBBERING: Dutch.

GRAYSON: Dutch. But when you went to school you learned English, French, and German?

NIBBERING: [Yes], that was in high school.

GRAYSON: In high school? Well, of course, German was not as hard to learn as French and English?

NIBBERING: No, as a child I don't . . . I have not had a problem with that. I mean, to hate the Germans—I don't like to have that in an interview because I have very good friends, also, in Germany. But, now, that feeling I didn't have. The teacher in German language was a good teacher. In some ways, this teaching language was—well, and grammar—it was like mathematics for me. You could say *in der*, *in das*, *in dem*, you know, all these kind of things. You don't have that in English. So, now, there were no bad feelings from my side. Perhaps I didn't realize enough. That is another thing, of course.

But, okay, the decision was made to take beta. And so, I had two teachers at high school—they were all very good, Mike, they were really very good. But the teacher, Simons [. . .] that was the teacher in mathematics and physics. That was an excellent teacher, so that motivated me more and more into the beta sciences. And then I have another teacher, Mensink [. . .]. He was the teacher in chemistry.

GRAYSON: And, I guess, most of these guys have been a very strong influence on you?

NIBBERING: They were, again, instrumental for me to say I have to take that part of science. Not biology . . . we had also, of course, biology, you know that. But they were attracting . . . well, studies. But they educated us, especially Simons, in a way that you did the final examination and we were prepared for a university study. At that time, if you took *gymnasium*, that was followed by university. You were simply prepared for an academic study. And I must say I made a choice to go to the University of Amsterdam because that was close to Zaandam. You know, it is a very small country. <T: 30 min> So I stayed with the uncle and aunt and went by train—or by motorbike, later—up and down to Amsterdam.

GRAYSON: How far was that?

NIBBERING: That's about 15 to 20 kilometers, one way. I had to cross the North Sea Canal. That was a canal made [. . .] a long time ago, between Amsterdam and [the harbor at] IJmuiden [Netherlands], I think at the end of the year 1800, or something like that. [. . .] There was a canal made—I don't know the year in which that was made—between Amsterdam and IJmuiden, to get ships from the North Sea to Amsterdam. Because in the past, if you go back the [Dutch] Golden Age, then ships came to Amsterdam via the North Sea. They had to go north from the Netherlands and then go into the South Sea and that was the way to get to Amsterdam. But when that canal was made then they could directly come from the North Sea into Amsterdam.

GRAYSON: Ah, okay.

NIBBERING: So made the choice for the University of Amsterdam. But then the director, also, he came in. I remember that in the last class of the *gymnasium*, those who were interested but didn't have, let's say, the money to pay to enter the university, you could get forms [that] you could fill in, and then send it to The Hague, [Netherlands], to the Ministry of Education, [Culture], and Science, ask for, and get, an open grant. *Renteloos voorschot*: you could get money, you didn't have to pay interest for that. It was a loan. Then you could start to study, and then if your study was over then you could pay back because then you would have a job, debt loan from the government. So I did it, so I asked for a *Renteloos voorschot*.

GRAYSON: Oh no. [laughter]

NIBBERING: [. . .] Well, *renteloos*, so it means a loan. But you don't have to pay interest. But I can spell it if you want. [. . .] So that was a pre-payment. They said, "Okay, here you have the money."

GRAYSON: Right.

NIBBERING: "Later on you will pay back."

GRAYSON: Okay. So what did it cost to go to school then?

NIBBERING: Now, I don't remember that anymore exactly. You had to pay in some fee, but there is another problem that I would like to mention to you.

GRAYSON: Well let's mention that.

NIBBERING: I sent it to The Hague, having filled in the forms. And but it had to be signed by a legal person. That was not me of course. No. I asked my uncle, Piet, Piet Konijn, "Could you sign?" And my aunt and my uncle they've always said, "Nibbie will do best." So they could not understand what was going on, but I filled it in and they signed because I will do it, okay, it will be okay. Nibbie was the nickname, Nibbie. [. . .] It's an abbreviation, of some way, from Nibbering. "Nibbie is doing okay." So he signed. And then I started to study at the University of Amsterdam but a few months later—and I think that was October, November '56—then a person, Fraase Storm, came along . . . and now I have to explain to you, it's a complicated story. I was on the children's protection organization.

My uncle and my aunt, they got money for that—for clothes, et cetera—and every year Mr. Fraase Storm, he came from the children's protection organization once per year to my uncle and aunt to discuss, of course, I was there. [. . .] And he was a nice man. But then he had a serious discussion with me. Because he said, "You went for studies to the University of Amsterdam." I didn't discuss that with the children's protection organization. That didn't come up in my mind to do that. And then he said, "But why not teacher—school for teachers," et cetera. And for me, that was strange. Because I decided myself, I thought. But he said then, "You submitted forms to The Hague, to the Minister of Education and Science, and that was not signed legally."

I said, “Not signed legally?” I said, “Uncle Piet signed.” I thought Uncle Piet is my guard. “Guard” is the right word, I think, isn’t it?

GRAYSON: Guardian.

NIBBERING: Guardian, [yes]. But he said, “No, that’s not true.” So, from my seven years until eighteen years I assumed that Uncle Piet was the guardian, but it was not true. So therefore I had false then . . .

GRAYSON: You violated the law.

NIBBERING: . . . violated the law in something. Then I noticed they had to pay longer for me because study will take time. And I noticed that. Then I said, “Oh, if there is a money problem that’s not a problem for me, because I will distribute newspapers.” Because I have decided to study at the university. That’s it. So I was a little bit stubborn.

GRAYSON: [laughter]

NIBBERING: Because my Aunt Neel, she was always for harmony. Because I thought the guardian . . . what do I have to do? I am here from seven years until eighteen, I’ve never seen him. So I said to my aunt when Fraase Storm was gone, “I wouldn’t like to see that guy because he has not shown up in eleven years.”

GRAYSON: [laughter]

NIBBERING: But my Aunt convinced me that I should nevertheless go. And I said—in the end I went by motorbike to the University, and then on the way back, then I went to the address where he lived in Zaandam. And of course I did ring: no sound, nobody there. I went to home, to the uncle and aunt where I lived, and I said to my aunt, “He wasn’t there and I will not go anymore. Over!” And after three weeks, I heard he had passed away, so I’ve never seen him. [laughter]

GRAYSON: So you had a guardian that you didn’t ever know?

NIBBERING: No.

GRAYSON: And but basically you were able to get out from under the problem because you said, “I’ll just go ahead and work.”

NIBBERING: [Yes].

GRAYSON: Did you have to then give up the loan?

NIBBERING: No, no, no. I continued to study, so the *renteloos voorschot*, I got. There is an additional thing, and then I think the story is more or less complete. Because I had not only to do with the Ministry of Education and Science but also with the Ministry of—how do you call it—judicial things, because of the children’s protection organization. I had two ministries that I had to deal with.

GRAYSON: What was the second one that you . . .

NIBBERING: Justice.

GRAYSON: Justice.

NIBBERING: Justice, I think it is.

GRAYSON: Okay.

NIBBERING: *Justitie*. Because the Ministry of Justice, they had to deal with these protection organizations. And I was the only one in the whole province of North Holland as a student at that time. Later on I heard that. Of course, Mike, I didn’t know that. I was the only one [with] this problematic situation. I had to deal with the Ministry of Education and Science and the Ministry of Justice.

GRAYSON: [laughter]

NIBBERING: Okay, but I did study, and that was okay, but then you had first your bachelor’s

degree. That was four years. A longer study than here in the United States. The average length of a study until your master's degree was about seven odd years. And, again, I must say it was a very good study, what I had at the *gymnasium*. The first three months I didn't have to do much at the <T: 40 min> University of Amsterdam. I had it from the teachers, Simons and Mensink. But you got a lot of physics and a lot of mathematics as you start to do chemistry.

GRAYSON: So did you decide when you started at the university that you wanted to pursue chemistry?

NIBBERING: No, not in the beginning.

GRAYSON: No?

NIBBERING: It was a general education. And then later on you decided more to specialize.

GRAYSON: Okay.

NIBBERING: But then the children's protection organization had—still, of course—to do with me, because I was not twenty-one.

GRAYSON: Ah, twenty-one was the age at which you could be . . . ?

NIBBERING: [Yes]. And so I heard, later on, that the idea that I would finish an academic study coming from a family, no academics . . . would he be able finish a study successfully? So, therefore, they said, "We'll continue the *renteloos voorschot* every year you go there," that at least my aunt and uncle. But they doubted whether I could make it. And then I did my bachelor's degree, *cum laude*. And *cum laude* is—I know in the United States you have *summa cum laude*, but in the Netherlands *cum laude* is really good. So then they said, "Probably he will get it to his master's degree." [laughter]

GRAYSON: Of course pretty soon you're going to be twenty-one, so you don't have to deal with them anymore. [laughter]

NIBBERING: No. But then they decided when I got my bachelor's degree, then I got rid of that. I had gotten a grant which I didn't have to pay back. That was nice, huh? And then I had

another three and a half years, and then I did my master's degree in chemistry, but specialization was physical organic chemistry. And that I can also explain why I made the choice. Because I had a very good professor in physical chemistry. His name was [Gerrit Jan] Hoijtink [. . .]. He was editor also of *Chemical Physical Letters*, I think. That I didn't know at that time. And he was at the Vrije Universiteit originally, but he came to the University of Amsterdam. And when I followed his lectures in physical chemistry, then, he explained bonding. We got molecular orbital theory, atomic orbitals combined to molecular orbitals, et cetera, et cetera. And these lectures were fascinating for me. You didn't have a syllabus, you know. Nowadays they say—well he recommended these kinds of books to buy and I did that. But a syllabus, written material, no. The professor gave his lectures. You made notes because you could not know—and then I wrote them out at home. And I still have them. But I thought, “Oh, now I understand chemical bonding. I will do physical chemistry with Gerrit Jan Hoijtink as the main study,” because you have to do that for almost one year.

But then he made the comment, “Theory is nice, but don't forget the experiment,” because, he said, “you now know from atomic orbitals that if you would have to predict which hydrocarbon is the most simple one, then it is CH_2 with an angle of 90 degrees.” But he then said, “You know that we have methane, natural gas from Groningen [Gas Fields],” and he said that CH_4 has four hydrogen atoms in an equal position around the carbon atom with an angle of 109 degrees . . . okay, the details he said are not important. Then he said nature doesn't know how to do that, but a human mind says to solve that problem. And realize this is a human mind experiment, we mix, now, orbitals. We mix s-orbital with p-orbitals and then we get sp^3 . The 1s down a carbon is the first. Then the 2s, two electrons and then the $2p_x$, $2p_y$, $2p_z$. And then he said, “Realize, if you do that, this is an <T: 45 min> artificial thing which the human mind is doing to get the problem solved.” Because if you do that then you get this tetrahedral structure of methane. Then he said so don't forget the experiment but now the thing is we cannot always get a hold of the molecules we would like to study. They are not available.

Then I thought, “Aha. So I have to mix physical chemistry with organic chemistry, because then I'm able to synthesize compounds, and then I can do theory.” That was the ideal, what I had in my head. So I decided to do physical organic chemistry for that reason. I went to Professor [Thymen J.] de Boer [. . .]. He was the physical organic chemist at that time. Before, there was another one, but Professor de Boer was, at that time, the physical organic chemist. So I went to him via the secretary—it was very official, Mike. It was Professor de Boer, and you could not [say] Mr. de Boer, Professor de Boer. And I learned when he retired, then, to say Thymen, because that was his forename. But before that, you could not say Thymen, it was Professor de Boer, all the time. [. . .] So he said, “Okay, next week you come back and you will get a project,” because I asked for a project which will be a combination of theory and experiments. That's understandable from the story.

GRAYSON: [Yes].

NIBBERING: And you had to show up at half past ten on Monday, via the secretary, and I

came in his room. And then he gave me the project of 1-nitropropane to show that the molecular ion of that compound—I didn't know what a molecular ion was at that time—underwent the McLafferty rearrangement. Because that had been shown for carbonyl compounds, aldehydes, ketones, acids, esters, but not for nitro groups, and he was a nitro specialist, and an NO₂ group is isoelectronic within the carboxylic group. So that was one thing, so I had to learn about mass spectrometry myself. He said the way is to put labels in it, deuterium labeling, so you label the 1-nitropropane specifically in the alpha position, in the beta position, in the gamma position. You had to synthesize these compounds and then do the mass spectrometry experiments.

So then I started my master's degree study. That means that it's for your specialization—one year. So I made these compounds and measured them with a single focusing AEI [Associated Electrical Industry] MS2H mass spectrometer. AEI is from, as you said, the electrical industries—you know that, I think—and MS2H it had a heated inlet system, but single focusing, only a magnet. And, well, it took, of course, some effort to get these labeled compounds because he also had said to me you are not allowed to use more than thirty guilders of D₂O. The amount of D₂O were then thirty guilders and it was not much.

GRAYSON: [. . .] Guilders?

NIBBERING: Guilders, [yes]. And a guilder . . . nowadays if you say [. . .] a euro is actually 2.2 guilders.

GRAYSON: Okay.

NIBBERING: So you see thirty guilders was less than euros euro. And a dollar at that time was, of course, around more than three and a half guilders.

GRAYSON: So he was, kind of, tight with the money?

NIBBERING: [Yes], was tight with the money. But you can understand that, because '56 was eleven years after the Second World War. The labs were not—I mean, the MS2H, that was expensive equipment for a lab of organic chemistry.

GRAYSON: [Yes]. <T: 50 min> So what could you buy with that? A couple of hundred milliliters?

NIBBERING: I don't remember anymore, no, not much.

GRAYSON: No.

NIBBERING: Because I have to practice the synthesis. Because—especially if you have to make $\text{CD}_3\text{CH}_2\text{CH}_2\text{NO}_2$, then you have to start, for example, with CD_3I , and then try to extend the chain, and in the end you get, then, $\text{CD}_3\text{CH}_2\text{CH}_2\text{I}$ and then make the nitro compound. And with every step you lose.

GRAYSON: Oh [yes].

NIBBERING: So you had to practice with unlabeled compounds, and then purify by simple GC [gas chromatography], and then if you have done it so many times then you thought, “Well now I can do it with the labeled compound,” and I can say to you, then, at the critical experiment you lost a lot, so the yield was lower, et cetera so that . . .

GRAYSON: [laughter]

NIBBERING: Okay, but in the end I made it. And Professor de Boer was a man who simply said to a student, “So, go on.” Sometimes you did see him, but you didn’t ask so much, because my supervisor was, in the end, Professor de Boer, but I had Henk Hofman. He was, at that time, the head of the mass spectrometry division . . . Henk Hofman. [. . .] He was running the mass spectrometry division of the—well, spectrometry department, because we had, also, NMR [nuclear magnetic resonance], the HR-60 from Varian, [Inc.]. You had ultraviolet equipment, you had infrared. And then Piet van der Haak is the name which I would like to mention, was head of the whole department for spectrometry. [. . .]

GRAYSON: He was kind of like the head cheese of the analytical, instrument . . .

NIBBERING: You could—we didn’t call it an analytical. It was the spectrometry division of the organic chemistry lab.

GRAYSON: Okay.

NIBBERING: But then, I remember that I went through the corridor and did see Professor de Boer, “Professor, it is true, the McLafferty rearrangement is there. It’s proven by deuterium

labeling, but there are more things.” And so we wrote a paper on that.³ There were, indeed, more observations, interesting observations. For example, I had seen that, also in that experiment, the loss of an OH radical from a molecular ion, and that OH radical contained a hydrogen atom from the methyl group. So you had the molecular line was at 89, very weak, *very weak* with electron ionization. They called it, then, electron impact, but now electron ionization is the right word. Then you have the peak at mass 72, and then we could show that was due to the loss of OH containing the methyl hydrogen from the labeling. And then, in addition to that, we had a stepwise scheme. Hydrogen atom transfer from the methyl group to the oxygen atom of the nitro group, and then there was either the root OH loss or ethylene loss, and the ethylene loss was the McLafferty rearrangement. But we did show it stepwise, because of the fact that we did see OH methyl hydrogen containing was

As an organic chemist, I must say, Mike—because in mass spectrometry there was a lot of discussion whether the reaction was stepwise or concerted. And I didn’t have a problem, because in the organic chemistry lectures it was very common that a reaction occurred in a stepwise fashion. Concerted was actually a little bit more difficult. We published that. I must also say, after the OH gamma, if I may call it a gamma loss, then there was a loss of water. And if you can . . . you are a chemist from origin or not?

GRAYSON: Not really.

NIBBERING: Not, no, okay, but you end up with a $\langle \text{T: 55 min} \rangle \dot{\text{C}}\text{H}_2\text{CH}_2\text{CH}_2 \dot{\text{N}}^+\text{O}$, if you lose OH. You have a radical position at the end—a terminal CH_2 group—and a radical position at nitrogen. And as an organic chemist you immediately think bi-radical, so: close. No, that experiment, the labeling, said [that] after the loss of OH, you had loss of water that contained only the hydrogen atoms next to the nitrogen. So that said no ring closure. And at that time we could not study it further, but simply we wrote the paper in the *Recueil des Travaux Chimiques des Pays-Bas*, that is in June . . . you have the publication list, so you will find it.

GRAYSON: Okay.

NIBBERING: *Recueil des Travaux Chimiques des Pays-Bas*, it’s the first one I think.

GRAYSON: It just says the abbreviated

³ N.M.M. Nibbering, Th.J. de Boer and H.J. Hofman, “Mass spectrometry of nitro compounds. Part I: Mass spectra of α -, β - and γ -deuterated 1- nitropropane,” *Recueil des Travaux Chimiques des Pays-Bas* 84 (1965): 481-487.

NIBBERING: [Yes], *Rec. Trav. Chim. Pay*

GRAYSON: Okay.

NIBBERING: The foreigners always said “*The Records of the Traveling Chemist.*” [laughter]

But then I wanted to go into industry after my master’s degree. My master’s degree was also *cum laude*. It went all well. But then Professor de Boer said to me, “You can go up for a PhD.”

Well, I thought, if the professor is saying that I can do a PhD, why not? [laughter] And so I started to do my PhD.

He said, “Well if you put some phenyl groups, or aromatic rings, in the chain, then phenyl alkyl nitro compounds,” he said, “you can make a thesis then out of it.” I started with that, and the idea was labeling, but then we caught hold of an AEI MS 902 mass spectrometer. [Fig 2.] That was a new instrument in the lab, so you could do high resolution measurements, you could more easily observe metastable ions. I worked for my thesis on that subject, making, of course, also the labeling compounds. But all the intermediate compounds which were made to make the nitro compounds, I also took the mass spectra. I remember also that Professor de Boer was not always checking how you did, but if he came along, then he said, “Oh what are you doing?”

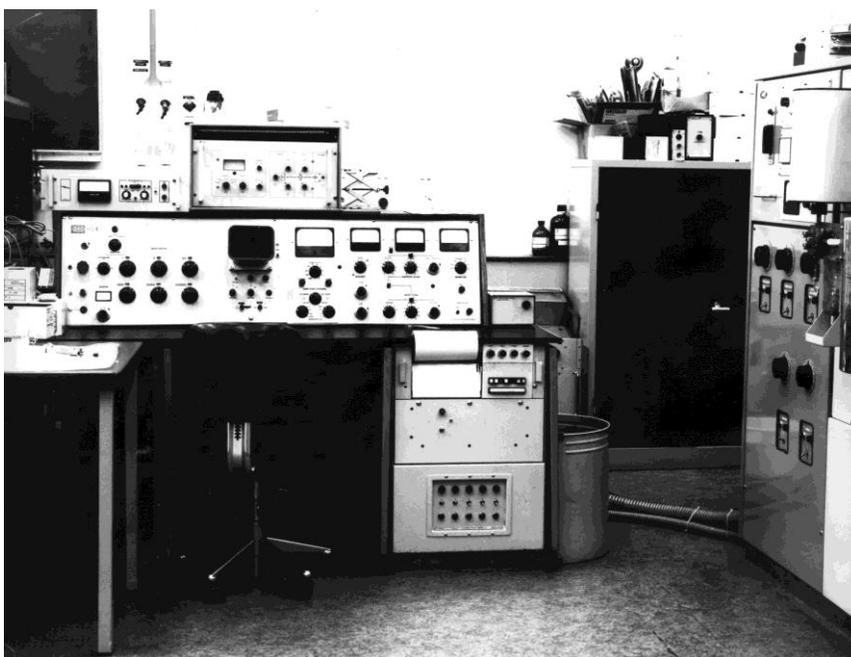


Figure 2. AEI MS 902 double focusing mass spectrometer from the University of Amsterdam

And I said, “Well I am now looking at phenylethyl alcohol,” for example.

And he said, “But we didn’t agree on that to do that.”

Then I said, “[Yes], Professor, but I have, now, the labeled compounds and these have not been studied before, so” And then he went away.” [laughter]

I think he was like van Oerle, the headmaster. He looked at the students and then knew, “Oh, we will make it.”

Because when he had retired I said to Thymen, [. . .] “Thymen, you were a little bit loose with the PhD students, you didn’t coach them so”

“[Yes],” he said, “My attitude was, you throw them in the middle of the ocean, and if they can swim they will reach the beach, and if not, oh [yes], sorry for them.” [laughter]

GRAYSON: Okay.

NIBBERING: But I must say that all his PhD students did very well.

GRAYSON: They learned how to swim.

NIBBERING: They learned how to swim. I worked for my thesis and then my predecessor—Henk Hofman, mentioned earlier—he finished his PhD, and he left the university and joined Unilever [N.V.] in Rotterdam, [Netherlands]. So, that was a vacant position, but I had in mind I’d go to industry. I had, in the midst of my PhD, discussions with the Royal Shell. Lab in Amsterdam. Royal Dutch Shell [plc] Lab is the official name, I think. And with [Koninklijke] Philips [NV] in Eindhoven, [Netherlands]. These interviews were really . . . now, very well. I mean, it was a pleasure to talk there with the people. And they said to me, “Oh you are on your PhD, and so much time you still have to do, give a sign when you are one year before,” because they would like to have me. If I would have made a decision at that time, then I would have <T: 60 min> chosen Philips. But they were almost equal, Shell and Philips. But when my predecessor left, then two permanent staff members tried to convince me that I should apply for that vacant position for the mass spectrometry division. And I said—Mike, stubborn as I am—“No, I go in industry.” No, I go in industry. [laughter] In the end, it was Piet van der Haak, one of them who said that I should apply, and another one was Jacques [M. H.] Dirx. So they both were working on me, and in the end I said, “Okay, I will go to Professor de Boer and Professor [Hendrikus O.] Huisman.” Professor Huisman was a synthetic organic chemist and Professor de Boer, physical organic chemist. And they interchanged their position every two years. So de Boer was, for example, at that time, adjunct director, and then Huisman was the director, and

then two years later they interchanged. So I came in the room of Professor Huisman [. . .] where Professor de Boer was also and . . .

GRAYSON: de Boer is the?

NIBBERING: The physical organic chemist.

GRAYSON: And we have his name for the record.

NIBBERING: Of course, [yes]. They were happy that I came. I could notice that. So we had an interview about how did I see the future for mass spectrometry, how would I operate and—because you had to do analysis for the organic chemists. They made organic compounds and you had to check that with mass spectrometry. And then I said in a very natural way—because it was not really planned by me, but a natural reaction—I said, “To do a high-qualified analysis, I think we should do research, also.

“Well, what do you mean?”

I said, “Well, to do research means that I need a group of, let’s say, three PhD students.” Whereas I myself had still to receive my PhD.

And they said, “Oh, that can be arranged.” It’s as simple as that. So in that way I became head of the mass spectrometry division, had to work on my PhD, and then soon after I started to coach PhD students.

The PhD there was four years, so Professor de Boer came in sometime and said, “How are you doing Mr. Nibbering?”

And I said to him, “Well, Professor, I am not doing so much.”

Then he’d go, “What do you mean?”

I said, “Well I am working, of course, in daytime on the analysis of organic compounds and to interpret spectra. But on my thesis I can only work in the evening and the weekends.”

“Oh,” he said, “It’s a question of finding the right balance,” and then he went. [laughter]

GRAYSON: Really helpful.

NIBBERING: But I don't want to give an impression that de Boer was a bad professor. On the contrary, he was an extremely good professor. So I made my thesis instead of four years, four and a half years. Well, that was reasonable. And then I got a Shell [Research Chemistry Prize]. Oh [yes], and for my master's degree I got a Unilever Chemical Prize. That is written down in my curriculum vitae. And for the PhD thesis, the Shell Research Prize.

Then, of course, Mike, you can imagine—because I never postdoc'ed. You understand now why, because I was ahead of the mass spectrometry division, so you could not go for a year away.

GRAYSON: Right, you had to go to work right away.

NIBBERING: But the Shell Research Prize, that was a very important prize.

GRAYSON: These were prizes . . . was there financial . . .

NIBBERING: [Yes]

GRAYSON: So it's more than just a recognition?

NIBBERING: No, no. It was really money added to that. And they said, I think, it was a prize which allowed you to be for three weeks in the United States.

GRAYSON: Oh.

NIBBERING: If you would take . . . well good accommodation, according to Shell standards,. But I said to my wife—we were married in '64—I said to her, “You could also make a choice for Europe,” <T: 65 min> and I said, “Europe, we can always do by car. How many times will we cross the ocean at that time? Rarely, I think, so let's go to the United States.” But we made, instead of three weeks, nine weeks out of it because we stayed overnight in very simple motels. Well for America's standard it was really simple and for us it was very luxury. [laughter] And that trip is completely . . . I don't know how my mind is working but I can reproduce that all the time, completely, what happened. The first was of course a long flight, and the first man I faced—I must say I had chosen from the literature of course the colleagues working in mass spectrometry in the United States. In Europe I started to be interested, et cetera. So I made a list, whom I would like to visit. And that list was handed over to Professor de Boer, then Professor

de Boer sent it over to Shell. And Shell was not controlling to whom I went. They were not saying, “You have to go to there.” That was my decision, that was the prize. But they wanted to know, and if they then did see, “He is visiting him in the neighborhood with somebody else,” they said, “Oh, perhaps you could also visit.” In that way the first man was Frank [H.] Field.

GRAYSON: Oh wow.

NIBBERING: And so Linden, New Jersey.

GRAYSON: Oh, sure.

NIBBERING: Where he had his chem ionization mass spectrometer. I know that Frank Field passed away recently. He was a gentleman, we had a very good time. Then Shell said if you are in Esso [Research and Engineering Company], Linden, New Jersey then also Graham [C.] Wanless because he did field ionization.

GRAYSON: Graham?

NIBBERING: He was the physical—the field ionization man.

GRAYSON: [Yes]. But neither of these people knew you from anybody?

NIBBERING: No, no, I picked them up from the literature because we’re . . .

GRAYSON: But they didn’t know you.

NIBBERING: No, no, no, no, Fred [W.] McLafferty knew me.

GRAYSON: Okay, but Frank Field didn’t, did he?

NIBBERING: No, no, because in ’67 that was the first time that I went to a triennial meeting and it was held in Berlin, [Germany], organized by Hans [D.] Beckey.

GRAYSON: Oh, okay.

NIBBERING: Then I met, of course, an American—the American said, “Oh, I think that Frank was there”—but as a PhD student in ’67 at the triennial meeting in Berlin. Then I met, of course, these people, but you can also imagine—do you learn to know these people, more or less? That’s also But that was a memorable meeting in Berlin, Mike.

First, professor de Boer accompanied me. My wife joined me in that trip.

GRAYSON: This was nineteen sixty . . .

NIBBERING: Sixty-seven. Before that time, I had met [Carl] Djerassi, Dudley [H.] Williams, at a meeting in Oxford, [England], but it was a local meeting. But in Berlin that was the International Mass Spectrometry Conference—the [fourth] one. Now, next year there will be the Twentieth International Mass Spectrometry Conference in Geneva, [Switzerland], and last October we had the Nineteenth International Mass Spectrometry Conference in Kyoto, Japan. But I have always attended these International Mass Spectrometry Conferences. Now it is going on in a scheme of every two years, but until now it was every three years.

GRAYSON: Three years.

NIBBERING: So I’ve met, of course, scientists. But the ones who I visited in ’69, they were not all there in Berlin. They didn’t know me then, of course, and I only knew them from the literature.

By the way, when I presented part of my PhD work in Berlin, then, the night before, I had ear problems. Very painful. As a child I had also that—I had problems. I know that my wife said there was a medical congress, for medical people, in that hotel. A medical person had been to look at my ears, and the next day I was more or less a little bit deaf. Professor de Boer was a little bit concerned whether I could present the lecture, and I said, “There’s no problem of course.”

But he said, “You should instruct the chairman,” and that was Klaus Biemann.⁴

⁴ Klaus Biemann, interview by Michael A. Grayson at Alton Bay, New Hampshire, 29 August 2006 (Philadelphia: Chemical Heritage Foundation, Transcript #279).

GRAYSON: Oh, okay.

NIBBERING: And he said, “You should instruct the chairman that you are not hearing so well if they pose questions.” Oh, okay. <T: 70 min> So I presented the lecture there, and it was on gamma-phenylpropyl bromide and alcohol, and we had seen some funny exchanges between the side chain in the ring and the molecular ions. Then after the lecture, the first man who stands up was Fred [W. McLafferty] and he started to congratulate me and I didn’t understand of course what he meant.⁵ He said that I had proven that . . . well he didn’t name the McLafferty . . . he pointed out that gamma hydrogen . . . that I had proven that it was stepwise because of the exchange. And he asked me whether I agreed with that and I said, “[Yes], but I have a better example,” stubborn again, “1-nitropropane.” From my master degree study. Well he didn’t agree. [laughter]

And then Djerassi, Siebl, Williams, they all were asking me questions. I’m not doing this because I’m so good, Mike, no, no, no. I liked it, of course, and in a natural way [. . .]. And so de Boer was impressed, so then he said to me, because it was in ’67, “Now you can finish your PhD.”

And believe me, I said, “Professor, no. Because that, and this, and that should be done. And then it is ready.” [laughter] Now I would say, “No, no, I’ve never been a person like in a calculating . . . no.” But stubborn. I say, “No, no, no, then it is ready,” instead of saying [yes], the other way around.

But then coming back to the trip to the United States: after Frank Field and having spoken with Graham Wanless, then we went to Ed [Edward R.] Thornton in Philadelphia, [Pennsylvania]. That was important, Mike, because there we did see the first big instrument in a flat . . . well it was a big instrument where the ion beam was deflected in the horizontal plane. I think it was the [Hitachi] RMU double-focusing mass spectrometers.

GRAYSON: [. . .] That was the Japanese.

NIBBERING: It was a Japanese machine.

GRAYSON: From . . .

⁵ Fred W. McLafferty, interview by Michael A. Grayson at Cornell University, Ithaca, New York, 22 and 23 January 2007 (Philadelphia: Chemical Heritage Foundation, Transcript #352).

NIBBERING: Hitachi [Ltd.]. [. . .] So that was an important thing, and by . . .

GRAYSON: What lab was that in?

NIBBERING: That was in Philadelphia with Ed Thornton. Ed Thornton.

GRAYSON: Ed?

NIBBERING: Ed Thornton [. . .].

GRAYSON: Thornton, okay.

NIBBERING: I think Michael Gross had been postdoc for some time with Ed Thornton.

GRAYSON: Oh.

NIBBERING: A physical organic chemist.

GRAYSON: Okay, and he was at what school?

NIBBERING: Philadelphia, University of Philadelphia.

GRAYSON: University of Pennsylvania?

NIBBERING: Pennsylvania, [yes]. In Philadelphia. And then I went to Maurice [M.] Bursey, at that time, in North Carolina, Chapel Hill. And he had just finished his postdoc, I think, or was already more than a year in Chapel Hill. But he worked, also, with Fred McLafferty, so he knew Fred McLafferty very well. And there I did see drift-cell ion cyclotron resonance mass spectrometer from Varian. And then I became excited because, there, I found out, of course, ion-molecule reaction in the gas phase. So Maurice told [me] what they were doing, and I thought that's interesting so you can study reactions of ion with molecules without solvents, and

that is important for physical organic chemistry. It was very inspiring and motivating. Later on, of course, I heard that [J. L.] Jack Beauchamp had these kind of machines.

And we visited the research [Research Triangle] Institute in Durham, [North Carolina], I think that was near to Chapel Hill, with a man named David Rosenthal.

GRAYSON: I remember David.

NIBBERING: You remember him?

GRAYSON: [Yes].

NIBBERING: It was also very stimulating, and from there I went to Bob [Robert W.] Kiser in Lexington, Kentucky.

GRAYSON: Oh [yes], Bob.

NIBBERING: Well they were all nice, the colleagues. But Bob Kiser was <T: 75 min> certainly a very friendly person. And he was working on scanning electrostatic and magnetic field scans. I remember that—computerized—and, I will say, after the tour, [it's] what I did in Amsterdam, of course. But I had a good time.

And from there I went to Sy [Seymour] Meyerson.⁶

GRAYSON: Sure.

NIBBERING: At the American Standard Oil Company [Indiana]. Later on, Sy had been, also, in Amsterdam, but that was the first time that I met Sy Meyerson, in the lab. And, you know, why was Sy on the list? Because of the tropylium ion. Simple as that.

And then I visited, also, Bill [William H.] Pirkle in Urbana.

⁶ Seymour Meyerson, interview by Michael A. Grayson at Gary, Indiana, 7 March 1991 (Philadelphia: Chemical Heritage Foundation, Transcript #398).

GRAYSON: Bill?

NIBBERING: Pirkle. [. . .] In Urbana-Champaign, Illinois. Because he was an organic chemist doing mass spectrometry, but also NMR, on—as far as I remember—these were also chiral compounds. An organic chemist is, of course, attracted by these kinds of things.

And from there I went to Thomas [H.] Kinstle in Iowa. Ames, Iowa. [. . .] That is also in the *Mass Spectrometry Review* paper I wrote, so you can find it there.⁷ And Thomas, the trip was organized by American Express in Amsterdam and I gave all these addresses where they had to go and also had many—well, at least one lecture that is someplace, sometimes three lectures. So, they said at the American Express office in Amsterdam, “Listen, the program is too overloaded. You should also take time for yourself.” [laughter]

Okay. Thomas Kinstle, and from there we went to Peter Brown in Phoenix, Arizona. But then we flew to Denver, [Colorado]. I didn’t know, at that time, Chuck [Charles H.] DePuy or Ronnie [Veronica M.] Bierbaum. But we rented a car. It was simple, Mike, at that time in the United States you came with your ticket and said, “I would like to change the ticket. Can I give it in and then rent a car?” And we drove, then, from Denver to Phoenix, so we did see Arches National Monument [Arches National Park], the Goosenecks [State Park]. It was a nice trip.

And now let me also mention a story in that one week that we were tourists. So we went to Arches National Monument. It was the end of May, nice weather, but there were not many visitors. I had a car with a plate from Holland, Michigan. No, Oregon. The Holland, Michigan, will come in. So, Oregon. And so the car was parked there and then a couple from LA, Los Angeles, [California], was there, we found out, because they said, “Hey, you’re far away from Oregon.”

I said, “No, we are from Holland.”

“Holland, Michigan?”

“No, no,” I said, “Holland—the Netherlands.”

“Oh, oh!” And then we started to talk, and that couple living in Los Angeles, they said, “[Yes], we know a man in the Netherlands,” et cetera. As if I would know all the Dutch. But he said, “He never replies anymore.”

⁷ N. M. M. Nibbering, “Four decades of joy in mass spectrometry,” *Mass Spectrometry Reviews* 25 (2006): 962-1017.

And I said, “[Yes], I was interested in motorbikes,” and I said, “Oh, Jacques Branse?” Believe me, really, they said, “Yes, Jacques Branse.” He did business but he was collecting racing bikes.

GRAYSON: Oh, okay.

NIBBERING: Racing motor bikes and he lived in Blaricum, in North Holland, but moved to Westzaan [Netherlands]. And so I said to that couple of L.A., “Sorry, that is Jacques Branse, he changed address.”

So you could see we were one of the twelve million people I think from the Netherlands, they were two of ten million, I think, were then in Los Angeles. You meet each other unplanned in [Arches National] park, and then you come to these kind of discussions. [. . .] Well he passed away many years ago.

GRAYSON: But basically they had been writing to this fellow and gotten no response?

NIBBERING: No reply, no.

GRAYSON: Now you’re going to tell them his new address?

NIBBERING: Because the motorbikes . . . I have always driven motorbikes and we were especially interested in racing bikes. So I still have one, and a 350 cubic centimeter Norton Manx with a Featherbed frame at home. But that’s another story of course.

GRAYSON: I bet it is, especially when you get it out and your wife sees you riding. [laughter]

NIBBERING: No, we went on holidays with a racing bike. Now you cannot do it anymore.

GRAYSON: That sounds interesting. What a coincidence.

NIBBERING: [Yes], coincidence, yes.

So we went to Peter Brown in Phoenix, Arizona, and, well, he was an organic chemist, but also a fan of fast cars. So that clicked immediately. [laughter] And from there we went to

UCLA [University of California, Los Angeles] to see David [A.] Lightner, who was a former PhD student of Carl Djerassi.

GRAYSON: David?

NIBBERING: Lightner [. . .]. But also Saul Winstein.

GRAYSON: Saul?

NIBBERING: Saul Winstein. [. . .] The well-known physical organic chemist. Because, why? Saul had been in Amsterdam to talk about his work on homotropylium ions.

GRAYSON: Oh, homotropylium?

NIBBERING: A CH₂ group in addition to the seven CH groups. So it's a flat ring, and the CH₂ group is a little bit out of plane. You keep the aromaticity. He presented that in Amsterdam, and then I had questions about it. And I said—that was during my thesis time that he was in Amsterdam—so I said, “I think we have, also, evidence for the homotropylium ion based on the labeling work.” Therefore I decided to visit him, of course. And I did write it down in the *Mass Spectrometry Review* article, but Saul said to me, “Why don't you come over to UCLA?” But I didn't do that, because you know now, if you become head of the department or division of mass spectrometry during your PhD, you get, also, the PhD students to build up your group and to make also the division of mass spectrometry more blossoming. You don't want to change job. I mean, nowadays you will think in another way.

GRAYSON: [Yes].

NIBBERING: From UCLA we went to Carl Djerassi. That was, of course, also logical. Carl Djerassi I have met in Berlin. You can also find it in the *Mass Spectrometry Review* article that I had to present my lecture in the evening. One of his co-workers was Alan [M.] Duffield from Australia.

He distributed, before I gave the lecture there, spectra to his students, the PhD students. Three. And he said this distribution, with following request, not now to do it, but look at the spectra, try to interpret it, write down how long it will take and why you came to the conclusion, et cetera. And then he said, “You have the word.”

And I said to Professor Djerassi, “Can I also participate in that? Can I get in a couple”

“[Yes], take it with you.”

“I will report when I am back in Europe.” Okay.

And my interpretation of mass spec—you can now guess why. I mean, working in an organic chemistry lab where you had to do the analysis, the organic chemist wanted to know not only the molecular weight, but also sometimes—some would say organic chemist, most of the time they say if the molecular weight is okay, then it’s okay—but if they would like to know more, then you would have to do the interpretation. And if NMR cannot solve it—it was a funny contradiction in their reasoning. They like NMR. It’s much simpler. Mass spectrometry was very complicated. But if NMR could not solve it then they came to mass spec and they thought that **<T: 85 min>** mass spec could solve their problems, whereas it was so difficult. That was a good training for me all the time to learn about fragmentation and to do research in that field also.

I came back later on in Europe and I did an interpretation. Well, in half an hour I managed to get proposals for the structures, and I sent them back to Djerassi. And later on there was a paper from Carl Djerassi and Joshua Lederberg from the Stanford University.⁸ There I found out that the compounds—he had given the elemental composition. So that one oxygen atom and one . . . you could figure out there was one double bond so that made already a selection in your mind. But the number of possibilities was more than 3,300—over that. [laughter]

Then how is the human mind working? So a colleague in the lab was doing, well, software development, Christ [W. F.] Kort, and he was really good at mathematics. [. . .] I said to Christ, because I thought it was artificial intelligence at that time, and I think they have published around six or eight papers, and I thought, “Oh that’s very interesting, because if you can do it by computer, that would be nice,” at that time.

So I said to Christ, “Christ, it would be nice if you could make a program.”

And he said, “Hmm. Okay, if you tell me how you do the interpretation.”

Then the problems started, because I said to Chris, “You look at the spectra and the number of bits which is going through your eyes is so large.” He immediately mentally said, “Oh no, no, that is not . . . no, no. So this, we’ll maybe narrow them down?”

⁸ Younus M. Sheikh, Armand Buchs, Allan B. Delfino, Gustav Schroll, A. M. Duffield, Carl Djerassi, B. G. Buchanan, G. L. Sutherland, E. A. Feigenbaum, and J. Lederberg, “Applications of artificial intelligence for chemical inference—V. An approach to the computer generation of cyclic structures. Differentiation between all the possible isomeric ketones of composition $C_6H_{10}O$,” *Organic Mass Spectrometry* 4 (1970): 493-501.

And I said to him, “There are many roads to get to Rome, [Italy].” That means you get so many ways to interpret.

He said, “If you say that, then I cannot make a program.” [laughter]

Now, from Carl Djerassi then I went . . . it was in the Bay Area. Well let’s say Stanford is a little bit outside the Bay Area but then to [Al] Burlingame, at the University of California, Berkeley, [California], and he was heavily involved the day when I visited him, because that was working on the NASA [National Aeronautics and Space Administration] project, first moon landing.

GRAYSON: Oh, boy!

NIBBERING: He was all the time in discussion with Houston [Manned Space Craft Center], because they had to collect rocks, and he was all the time apologizing. I met him now recently—last year in Kyoto, [Japan]. [Yes], that’s recently. It was nice to see him again. But he was coming along, apologizing, “No, you’ll actually . . . I will be there, professor.” And he says, “Okay, okay.” I got a nice picture of the Earth from space that I still have at home. He was at the lecture.

And then I also visited Phil [A.] Wadsworth from Shell [Development Company], Emeryville, [California]. Because now, you see, Shell knew the people that I visited, so they said why not Phil? Visiting Phil Wadsworth. Also a very pleasant visit.

And then we crossed the United States to go to Fred McLafferty in Ithaca, [New York]. And Fred wanted to have me as a postdoc. But that was impossible, of course. Later on I had been in Fred McLafferty’s lab, but that was for other reasons. I had been there for a few months, working, but let me first finish the trip to the United States of course.

After having a visit with Fred then the last man was Alex [G.] Harrison in the winter.

GRAYSON: Okay, I’m not familiar with that gentleman.

NIBBERING: Alex.

GRAYSON: Oh, Harrison?

NIBBERING: [Yes], Harrison.

GRAYSON: Oh the CI, chemical ionization?

NIBBERING: Well he did tropylium ions, also, and thermal chemistry, and he is now more on a, let's say, ions from amino acids and peptides. He changed, but he's a physical chemist and it was a very good colleague of also for Keith [R.] Jennings because Alex had spent also some time with Keith at Warwick University.⁹

And then back home.

GRAYSON: Basically they left . . . it was your discretion how to spend the money. So if you could stretch it out for . . .

NIBBERING: Nine weeks instead of <T: 90 min> three weeks.

GRAYSON: . . . nine weeks, then that was . . . they didn't care and that was . . .

NIBBERING: Oh no, no, no, no, no. They didn't . . . no, no, no. They didn't know about the time schedule.

GRAYSON: Oh, they didn't?

NIBBERING: They knew about the people.

GRAYSON: Oh, but they couldn't figure out that you were . . .

NIBBERING: No, I had a mentor at Shell that was Dr. [E. D.] Engelhardt. Dr. Engelhardt.¹⁰ [. . .] And he was at Rijswijk, Shell Rijswijk. Not in Amsterdam, but in Shell Rijswijk, which is the exploration lab. [. . .] And as the exploration lab of the Shell Company.

GRAYSON: Ah, okay. So he had some idea of what you were going to be doing?

⁹ Keith R. Jennings, interview by Michael A. Grayson at Leamington Spa, Warwickshire, United Kingdom, 24 and 25 April 2008 (Philadelphia: Chemical Heritage Foundation, Transcript #419).

¹⁰ Nibbering is referring to the Koninklijke/Shell Exploratie en Productie Laboratorium (KESPL) in Rijswijk.

NIBBERING: I had to write a report, of course.

GRAYSON: Sure.

NIBBERING: Now that was very exciting. I have it somewhere at home. I keep too many things, but there are also too many things. I know in which direction I more or less have to look at where it is, but I have, at least I think, still a good memory. I remember that I wrote that what I have seen during the trip was the drift cell ICR [ion cyclotron resonance]. I thought this was really a very good method to have for physical organic chemistry, because I expect there are a lot of results which will be of interest to the organic chemist. Therefore I wrote a proposal for the Dutch national science foundation, the chemistry division, but I could not submit it. It always went through the professor. That was the rule. So Professor de Boer, he looked at my proposal, and then might have changed some Dutch, et cetera. But he was in the organization of the [Netherlands Organization for Scientific Research]. Actually it was called ZWO [Nederlandse Organisatie voor Zuiver-Wetenschappelijk Onderzoek], that means pure scientific research. [. . .] That was pure scientific research [Netherlands Organization for the Advancement of Pure Research], now it is NWO [Nederlandse Organisatie voor Wetenschappelijk Onderzoek], the Netherlands Science Research [Netherlands Organization for Scientific Research]. [. . .] He came back, I remember, in my office then, and he said congratulations. Because I got . . . what was it, two-hundred fifty-thousand guilders . . . that means there was a quarter of a million guilders.

GRAYSON: Whoa!

NIBBERING: To buy the Varian Syrotron, drift cell ion cyclotron resonance mass spectrometer. It is I think V5903 was the . . . Varian V5903 Syrotron. [. . .] But it was a drift cell ion cyclotron resonance mass spectrometer, with an ion pump, getter pump. Well, I got that money so I could order that machine. Oh [yes], but de Boer also said to me, “Congratulations, and we expect, of course, many results,” and then he went again. [laughter]

GRAYSON: Right. Get to work!

NIBBERING: But I wanted also to do it because, since the trip, I read all the literature from drift cell ICR that you could do at that time. And I made, of course, a syllabus for teaching. But when we started to do research, if students came in, I gave them that booklet. It was printed. Perhaps I should have written—made a book out of it, an official booklet.

GRAYSON: [Yes].

NIBBERING: Okay, I didn't do that. So we had always a good start, and it was also a good entry to come up with a research project. Because you could say, "They said that in the literature. Oh, perhaps it is different."

GRAYSON: So probably at that time there weren't more than, what, a dozen papers? That were a dozen researchers?

NIBBERING: [Yes], not many. Jack Beauchamp of course.¹¹ <T: 95 min> Carl Djerassi had one.¹² But it took a long time to get it installed. We had a problem with the electricity that was found out. It was unstable, and they sent over technicians, but they could not solve the problem. And in the end they sent somebody who was well-experienced from Varian, California to Amsterdam. It was in Palo Alto, [California], of course. He managed to do it, but he found out the electrical environment was very polluted. A lot of noise. So we had to stabilize it, and then it started to work. But in the meantime, the thing was, of course, pumping all the time, and I tried to do experiments to learn to work with the equipment and how that worked. And the ion getter pump in the end didn't do it anymore, but the instrument was not fully paid. Of course I waited until it was approved. That is the normal way.

And then they said, "But you have worked at too high pressures." Well ten to the minus five, ten to the minus

And I said, "Listen, that is an instrument which was designed to do ion-molecule chemistry." So you do it a higher pressure. If you decide to have an ion getter pump, then perhaps that is not a good idea. In the end, they adopted my arguments because I said, "Listen, there will be a meeting on ICR in the lab of Keith Jennings," which was the other one in Europe. [Fig. 3 and 4] "And there will be a meeting and I will not keep my mouth—of course." I mean, why should I? And then I had gotten an ion getter pump, and then it was okay. Later on we changed it and there is, in one of the pictures you can see, we have mercury pump added to it to get rid of the . . .

¹¹ Beauchamp, Jessie L., Leslie R. Anders, and John D. Baldeschwieler. "Ion-molecule reactions in chloroethylene by ion cyclotron resonance spectroscopy." *Journal of the American Chemical Society* 89, no. 18 (1967): 4569-4577.

¹² Dickman, J., et al., "Mass spectrometry in structural and stereochemical problems. CLXIX. Determination of the structures of the ions produced in the single and double McLafferty rearrangements by ion cyclotron resonance spectroscopy," *J. Amer. Chem. Soc.*, 1969. 91(8): p. 2069-84.



Figure 3. Keith Jennings

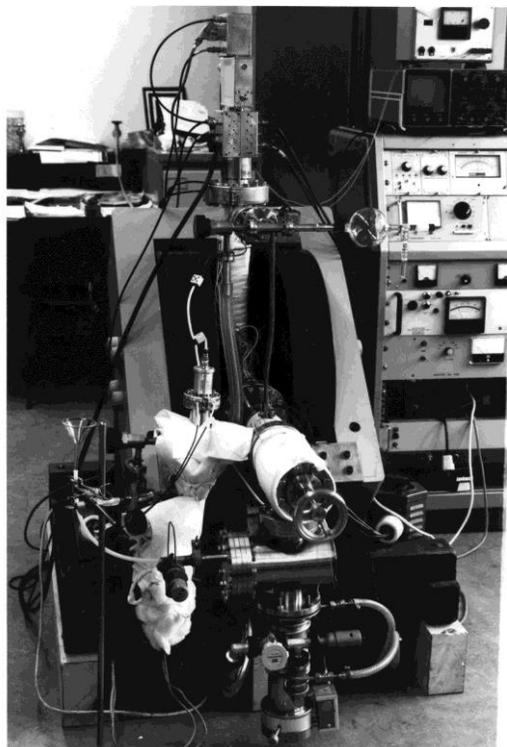


Figure 4. Pumping system of drift cell ICR instrument from the University of Amsterdam

GRAYSON: Well like you said, it's a silly idea if you're going to continue to work at high pressure to put a getter pump on it.

NIBBERING: I don't want to blame companies. I mean, they do their best also.

GRAYSON: I wondered if it—was Varian, maybe, in the ion getter pump business and they wanted to use them or something like that?

NIBBERING: That is the thing. Varian, I think, was more a company for NMR. I can imagine if you, as a company, start in another field, we have knowledge there that you sometimes say, well, let us put in that because we know companies in their area. That can happen of course.

Oh, by the way, when I visited Djerassi, [. . .] I spoke with Bob [Robert E.] Finnigan, then. He was working on the campus with [T. Z.] Chu, I think was his co-worker.¹³ I suspect that you know him.

GRAYSON: [Yes].

NIBBERING: That was also nice because they were working on the . . . what was it . . . the quadrupoles, I think, isn't it? Bob Finnigan.

GRAYSON: [Yes], quadrupole.

NIBBERING: He had visited, also, me in Amsterdam later on. But it was nice because later on you could see Bob Finnigan. Finnigan MAT [Ltd.]. [. . .] You see that, from the trip to the United States, it paid off very well. Scientifically, it was a very interesting trip, and it introduced me to drift cell ICR.

GRAYSON: It worked both ways, I think, for people on both sides. And then it was a very good use of this Shell award.

¹³ Robert E. Finnigan, interview by David C. Brock at Los Altos, California, 4 December 2001 (Philadelphia: Chemical Heritage Foundation, Transcript #227).

NIBBERING: Shell Research Chemistry Prize. No, the Dutch Shell Research Prize. It is written down in the review again. Because I'm precise what is written down so that I am really telling you the truth. [laughter]

GRAYSON: Okay, sure.

NIBBERING: It's exactly as possible.

GRAYSON: Sure, sure. Have you gotten your PhD by this time yet or are you . . . ?

NIBBERING: My PhD was—because the trip to the United States was made after my PhD.

GRAYSON: Okay.

NIBBERING: My PhD was done on the second of October, if I'm right. I think that is right, in '68. We were started on the first of April in '64.

GRAYSON: Okay.

NIBBERING: So it was a little bit longer than four years. Because the prize was awarded for the PhD thesis.

GRAYSON: Right, okay.

NIBBERING: You see?

GRAYSON: Very good. Now in European tradition they <T: 100 min> usually have this—at least in Germany—this period after a PhD if you went into an academic environment, you had this . . . I can't think of the name of it now in German. It's kind of like a . . .

NIBBERING: *Habilitation.*

GRAYSON: Oh yes, the . . .

NIBBERING: No, no, we don't have that .

GRAYSON: You don't have the *Habilitation*?

NIBBERING: No, no, no, we don't have that. Our oldest son [Erik T. J. Nibbering] is working in the Max Born Institute [Max Born Institut für Nichtlineare Optik und Kurzzeitspektroskopie]. He decided to study at the Vrije University because he learned, when we in Boulder, Colorado, in 1980—that is a later period of course. But then the American colleagues said, if you go to a university, don't go to a university where your father is professor. Oh [yes], the Netherlands is very small, you know.

GRAYSON: [Yes].

NIBBERING: But he decided therefore—because we never coached the children what to do. I said if they can find it out themselves, why not? It's better. Perhaps like de Boer, hey?

GRAYSON: Right. [laughter] Same thing.

NIBBERING: Same thing.

GRAYSON: Swim. [laughter]

NIBBERING: [Yes], swim. But he decided to do chemistry at the Vrije Universiteit in Amsterdam, master's degree, cum laude also, physical chemistry, cum laude. And he took additional physics, and then he went to [Rijksuniversiteit] Groningen to do laser work with Douwe [A.] Wiersma, then he got his PhD there, also cum laude. I am very proud of it, the colleagues are saying that he's doing extremely well. Then he went for three years to France to work with [André] Mysyrowicz in Orsay [. . .] in a classified lab with very strong lasers, I think for military purposes. I had never been there because when we went to him then we want to see him and I thought, well, the lasers. And after three years he went to Berlin and joined the Max Born Institute where he is still working out there. Thomas Elsässer was then the director. He is there—the group leader—and independent, contrary to Max Planck Institutes, so he has his own

funding, et cetera, and therefore I know that colleagues say he is doing extremely well. But he did the *Habilitation* also.

GRAYSON: So he did in Germany?

NIBBERING: At Freie Universität in Berlin.

GRAYSON: Oh, okay.

NIBBERING: Because if you do that, Mike, then you can apply for professorships if there are vacant positions.

GRAYSON: Ah, okay.

NIBBERING: But they can offer you but . . . it's doing in Berlin, and Berlin is a very interesting city. It takes a lot of people from outside, all parts of the world. And if I say to you the University of Cottbus then you will say, "Cottbus? Never heard of it." Of course, that's border, Germany-Poland. It will not say that it must be a bad university but it is not a university which will attract. So if our older son will change positions then it has to improve or get better. Then you can think about Munich, [Germany], Hamburg, [Germany]. But okay, going back, of course, that is another story.

GRAYSON: So but in the Netherlands the *Habilitation* is not . . .

NIBBERING: [. . .] No, no. But you also know the reason why I didn't postdoc.

GRAYSON: Sure, because you've already had a job.

NIBBERING: In some way, I regret it, because I have been—later on—many times in the United States. And also, this week with Graham [R. Graham Cooks] is a very motivating group. So I see also, it is always good to be in other labs and have communications with other groups. But I can also say to you, well there are three things in mass spectrometry which are important, in my opinion, and these are time independent. That is, fundamental research is one pillar. The other one is developing of instruments and new methodologies is the second, and the third one is applications. And it doesn't matter in which time you live. The subject changes, but, [yes].

GRAYSON: That's a good assessment. And that's how progress is made.

NIBBERING: [Yes].

GRAYSON: So now you have had the opportunity to step right into academia without any further ado. Now do you have any teaching obligations in this position?

NIBBERING: [Yes], I have always taught spectrometry courses but especially mass spectrometry. And I have done, for a number of years but not many years, first-year organic chemistry. Well, I'm not saying that other people talk about me whether I did it well, but I did it extremely well they said. Now I have to believe. But why did not I teach so much? Because I did run the mass spectrometry division for the organic chemists.

That, of course—the interpretation, <**T: 105 min**> coaching the PhD students from other groups, telling them about mass spectrometry—Professor de Boer and Huisman, they regarded also as teaching. It was also true. But also, Mike, I said to Thymen de Boer, at that time of course, Professor de Boer, I didn't understand why you had these different labs. Like a lab of organic chemistry, a lab of inorganic chemistry, a lab of physical chemistry, and analytical chemistry, biochemistry. That was, of course, of finances that you have this organization. But I had done, already—very early in my career, then, and you can see it from the publications also for inorganic aluminium isopropoxides—found out about not only a monomer but there are dimer, trimer structure for . . .¹⁴ And also for chemical engineering, there was a group of chemical engineering and official chair. So I didn't see the borders between these labs from the mass spectrometry point of view. So it was applied in many other fields. That was the attractive thing also.

GRAYSON: So you had students as graduate students, and you also taught the classes [for] undergraduate students.

NIBBERING: [Yes].

GRAYSON: So were these—now you talk about organic chemistry, typically in America, those are large sections. Are these like cases where you had a hundred students or . . . ?

¹⁴ W. Fieggen, H. Gerding and N.M.M. Nibbering, "Structure and physical properties of aluminium alkoxides. 1. Mass spectra of aluminium isopropoxides," *Recueil des Travaux Chimiques des Pays-Bas* 87 (1968): 377-383.

NIBBERING: Oh, the first year, organic chemistry was attended by one hundred thirty people.

GRAYSON: Okay. So it's a typical organic chemistry thing, where you've got a . . .

NIBBERING: Nowadays it has come way down, understand that [that] diminished. But at that time, one hundred thirty for the first year of organic chemistry. And the mass spectrometry courses, they were more around twenty-five, thirty people.

GRAYSON: Okay, but that's a pretty good size group for mass spec.

NIBBERING: And then also what we did that was [. . .] you could choose for that, you didn't have to do that for your study. But you could make a choice for it like I did during my study. I attended lecture in other fields from physics, simply because I did want to know it.

GRAYSON: Sure.

NIBBERING: But then advanced mass spectrometry: so you told about the new chemical instrumentation, other methods, but then also the interpretation of spectra without much additional information, so not NMR or infrared, but simply mass spec. And then . . .

GRAYSON: Now this has all been electron impact.

NIBBERING: No, also chemical ionization.

GRAYSON: Chemical ionization.

NIBBERING: But, electron ionization, electron impact as you call it, that was the most—the biggest part of it, of course. Later on it changed and things were added, of course. You had also electrospray and MALDI [matrix-assisted laser desorption/ionization]. But the trick was to get to a structure only based on the mass spectra. And what is the principle of interpretation? You say it cannot be this because of that and that reason, it cannot be this because of that and that reason, and in the end you will say—because you excluded this and that and that, and that in the end—so it must be that.

GRAYSON: [. . .] Was there much use made of database searching and library spectra?

NIBBERING: We had that. We used it at the division of mass spectrometry. That was a way, I also told them . . . because the McLafferty—the Wiley [Registry of Mass Spectra Data]—250,000 which could be scanned in later on and in parts of a second. I said that was very handy for analytical purpose. Because it saves time.

GRAYSON: Right.

NIBBERING: Simple as that. But, I always said it's nice but it is comparing stamps with stamps. Now if it doesn't fit, if it is not in the database, then the person in question will still ask you, do you have an idea? No. Then the interpretation is coming in, so I think it is very important. I can assure you that with pharmacologists we had a problem that was the nice thing about the application part, you had not only with chemists, physicists came with the purity of their gases.

GRAYSON: [laughter]

NIBBERING: Then you had medical people also because we have not spoken about developments of ionization methods also in Amsterdam. <T: 110 min> But we did samples for hospitals in academic hospitals with field desorption. The eye disease—how do you call it?—glaucoma. But there was a pharmacology group at the University of Amsterdam and they had a compound, it was isolated from wasps which were in Egypt, and these wasps had the capability to inject their prey with some liquid and that paralyzed the prey, so they always had fresh food because of their own diet.

GRAYSON: You say wasps?

NIBBERING: [Yes], wasps, you know, these nasty—like bees, but it is wasp.

GRAYSON: [Yes], okay. Well we would call it [. . .] wasp.

NIBBERING: Well [yes], I think wasp, wasp. I took this [pen and paper] with me because I thought . . . I manage to speak English but it is not always . . .

GRAYSON: I think what you're referring to is what we would call is a wasp.

NIBBERING: [. . .] Okay, that's it.

GRAYSON: It's a flying bug that's . . .

NIBBERING: But in Dutch language it is a *wesp*.

GRAYSON: *Wesp*.

NIBBERING: That's the confusion. [laughter] And so, they had to kill I think at least two thousand wasps to get enough material. So they came to the mass spectrometry division and then they said, "Could you analyze it?"

"[Yes], okay." And then we took the mass spectrum. And I started to interpret, and I said, "It seems as if these are phenol compounds."

And these guys said, "Oh that could well be." Everything was possible.

But then, looking further, I said, "How do you purify, how do you get a sample?" And they used plastic tubes. I said, "Oh, oh, oh."¹⁵

GRAYSON: Okay. [laughter]

NIBBERING: So we had phthalates, et cetera, said, "Oh, now we have to do it another way." So they had to repeat that experiment. And then we had, in the end, enough compound to do an elemental composition, electron ionization, field ionization, the molecular weight was 243. It had, I think, eight or nine carbon atoms, one nitrogen, and an oxygen. We found out it was an amide, and then fully saturated alkane chain. And then, of course, the interpretation of that spectrum, no NMR. So by regular interpreting, as we did with the course, advanced course interpretation, there was a student from [W.] Nico Spekamp, synthetic organic chemistry colleague. So, it took me an afternoon and the student was there, so he could know how I did it and in the end I came up with four possibilities, was an amide, where the chain length could be

¹⁵ The phenol compounds were contamination from the plastic tubes.

one carbon atom or the other side, et cetera, and so they started to synthesize. It was not simple, because to check the activity of that and that synthesis was certainly not easy, as Nico Spekamp, the colleague said. But then the pharmacologist talked at a conference and then Dow [Chemical Company] heard about it. And Dow said, “Oh, that is very interesting.” And they offered to cooperate, and they gave, also, some funding, and in the end it was solved.

And in the end we had, also, enough sample to get an NMR spectrum. But my colleague, Cor [Cornelis] Kruk who did NMR, I said to Cor, “Now there’s another thing about NMR. NMR is easy for organic chemists because they know what they are doing, but now if you get a sample from that origin and you say to an NMR man, ‘Can you solve the problem?’ it is not so easy. Then it’s as difficult as mass spec.” But I gave him the molecular weight information and structure we thought, so that helps. But I said, in the end, to Cor, it might well be that they have managed to make their compound, they test it, it might well be that it is not as active as the natural isolated compound because we could see there were impurities. You know, the mixing of things can . . . indeed the activity was not as large as the natural one. I think it is—perhaps I didn’t write that in the *Mass Spectrometry Review* article, that particular paper, but okay, of course I covered as much as I could. But you see how it works from having done <T: 115 min> organic chemistry, physical chemistry, interested in structure—why?—and in a logical way, that has been the basis to do gas-phase ion chemistry. This is ion-molecular chemistry, of course, get your hands on fragmentations. And organic chemists of course, they said, “It’s nice but it’s all high energy chemistry. It’s nothing to do with . . .” But I always regretted in the first year they thought, of course: organic chemistry, always in solvents. And if you remove solvents, then that is not—amazing, but the chemistry is a little bit changing isn’t it?

GRAYSON: [Yes].

NIBBERING: And if you fire an electron, or seventy electron-volts in a molecule, organic chemists say, of course, “Seventy electron volts, that is a very strange unit. How many kcal is that?” and you say, “Well it’s about 1,500 kcal,” [yes], “Nothing will survive.”

GRAYSON: [laughter]

NIBBERING: So this is a ridiculous method, but then you say, “The electron is passing the molecule, so that it’s only part of the energies transferred.”

GRAYSON: [Yes].

NIBBERING: “[Yes], but how much?” Then you say 3 to 5 electron volts. But that is still a lot of energy, although carbon-carbon bonds are 80 kcal per mol. So more than 3.5 electron volts.

H-bonds are 4 electron volts. But, these guys don't think in these terms. But I must say after all the years of research in that field worldwide by many other colleagues also in that field, fortunately it has come down to it is not high energy chemistry. There are rules behind it. But we all know chemistry is very complicated. You take four elements: carbon, hydrogen, nitrogen, and oxygen, or add sulfur and phosphor. And then the number of possibilities of stable molecules, Mike, is terribly high.

GRAYSON: Oh [yes]. Definitely.

NIBBERING: That was exactly what de Boer always pointed out: with only this limited number of elements, that there are so many possibilities. So I always said, also, in teaching mass spectrometry, realize how many possibilities there are. Go to the Beilstein in the lab. You see there these thick books on all these different compounds, so don't expect that mass spec is also so easy. And then I said, also, to make program for interpretation, like a database set, it's almost impossible. Nowadays I would say there is more computer facility, of course, but the variety in chemistry is so large.

GRAYSON: Yes.[. . .] Definitely. So your teaching has been pretty much a little bit on the light side compared to what a normal academic professor would teach, but you did have an obligation in teaching students in both undergraduate and in the graduate area.

NIBBERING: [Yes].

GRAYSON: And so, where do you then . . .

NIBBERING: I did regard it as an obligation.

GRAYSON: Okay, but I mean the school did, right? I mean, did . . .

NIBBERING: No. I must say the course . . . the first year organic chemistry, but that was to help a colleague. I needed to replace somebody for some time.

GRAYSON: Okay.

NIBBERING: But now, now, because Professor Huisman and Professor de Boer, they did see

that I was very busy to coach the students in the sense that they had their problems and I had to tell . . . because they could not do it. And then the courses in mass spectrometry was of course [to be] written all my life, so to speak.

GRAYSON: Right. Now your graduate students that . . . how did they come to you? Did they . . .

NIBBERING: Oh, well they studied organic chemistry, and we were in organic chemistry, of course. And these people did, for example, master degree studies, and they got spectra from our division, I tried to explain. And we had a scheme in our lab: there were several professors, that included synthetic, bio, and physical organic. We had a number of PhD positions funded by the university. And that was discussed in the so-called committee for scientific research of the lab of organic chemistry. So you knew how many PhD students you should have on a more or less equal partition. If I had an open position, then either you made an advertisement—but many times you didn't have to do it. Because there were master degree students <T: 120 min> in the group of de Boer, for example, physical organic chemistry. And then de Boer said, "Well go to Nico Nibbering." For example, later on I will mention Leo [J.] de Koning for example. And Thymen said he didn't have a position for him. But he was not jealous of me but he said, "It's very good that you get him. He's a good student." But also from other labs, from the Vrije Universiteit, I got them . Because we did run also samples for other labs when they didn't have the sophisticated instrumentation because we had double-focusing mass spec, ICR, FT-ICR [Fourier transform ion cyclotron resonance], you know . . .

GRAYSON: So who paid for all that stuff?

NIBBERING: The thing is that I managed to get funding from the [Netherlands Organization for] Chemical Research. So you apply there, you submitted a proposal for instrumentation together with the project and that worked out—not easy, perhaps that can come later on. But I must say I got, always, good funding from the [Netherlands Organization for Scientific Research].

GRAYSON: Did you always—did you have only one source of funding? Throughout your career?

NIBBERING: Now let's say the [Associated Electrical Industries] MS2H was already there when I started. The MS9, I was not involved. The Varian MAT-711 was another double-focusing instrument with the Mattauch-Herzog geometry. Of course the MS9 was a Nier-Johnson geometry. You are familiar, I think, with the Nier-Johnson geometry?

GRAYSON: [Yes].

NIBBERING: And the Mattauch-Herzog, you will have heard about that. That Varian MAT-711 instrument, Mike, that came in the following way in our lab. [Fig. 5] Analytical chemistry and organic chemistry together, they want to have an additional instrument—in addition to the AEI MS9 because the AEI MS 9 was around 1966. And Professor Huber—J. [Joseph] F. K. Huber [. . .] he was a well-known analytical chemist in GC.

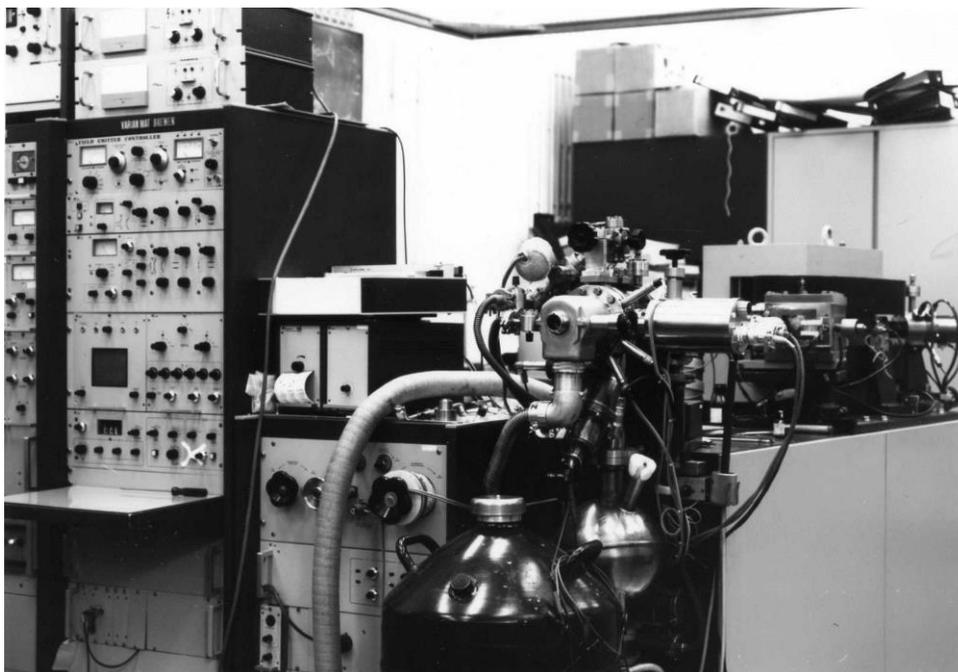


Figure 5. Console and tube unit from the Varian MAT-711 double focusing mass spectrometer at the University of Amsterdam

GRAYSON: Gas chromatography?

NIBBERING: But later on LC [liquid chromatography]. He also gave lectures at Harvard University. He was from Vienna, [Austria], came to the Netherlands, and via the University of Eindhoven he joined the University of Amsterdam. Joseph was his full name. He wanted to have a GC-MS instrument, and of course I was the logical man to cooperate with him. And I have a very pleasant memory about Joseph. It clicked, if I say it in English. So we said yes, a new instrument, and there were two hundred thousand guilder from organic, two hundred thousand from analytical and four hundred thousand guilders were provided from a special fund from the faculty and also the higher level in the university, but I didn't know. I mean, I didn't know the details, because Professor Huisman, at that time the director of the organic chemistry lab, he managed to get that money. And nowadays, Huisman, I like the man . . . de Boer and Huisman, they were a little bit fighting with each other—not really, but, I mean, their characters were a

little bit different. But Huisman, he had very good contacts also in The Hague, in the governmental level. I remember that he said, “It is arranged, you will get the instrument.” And some of the people from the physical organics said, “But has it been signed? Is there a contract?” He said, “No, it’s not required.” And it was true. Not required.

GRAYSON: Wow.

NIBBERING: And, well, I don’t want to go too far outside the family, but Hans [Nibbering], our second son, is in financial business. Of course we make contracts. There are sometimes also that you say we agree—we can trust each other. Trust.

GRAYSON: Right.

NIBBERING: Trust is the word. At that time that could be done. And so with the eight hundred thousand guilders it was almost . . . a lot of money. Then we made trips to AEI, MAT, VG, to come to a conclusion, what kind of instrument it should be. And in the end we made a decision, the Varian MAT-711. The MAT—Varian [Data Machines] was, of course, the computer system, 620i, <T: 125 min> coupled . . .

GRAYSON: When did you buy that?

NIBBERING: ’Sixty-nine.

GRAYSON: Oh, okay.

NIBBERING: The Varian 620i computer, data system. Joseph Huber said to me, “First, you work with the instrument and if you are satisfied with the set-up and it is installed and you have experience enough, then we will try to do GC-MS.”

GRAYSON: Oh, okay.

NIBBERING: But, before that time came then he had changed his interest in LC-MS.

GRAYSON: Ah yes, okay.

NIBBERING: [laughter] But this was a trip with him and Piet van der Haak who I mentioned before. We went to Bremen, [Germany], and there was also a technician with me, of course. But there was still money left of the eight hundred thousand. So we ordered electron ionization and the data system, et cetera, and then they said there is still thirty-five thousand guilders left. Joseph said, “What do you want?” I said, “Field ionization.” They brought me a field ionization because I had read the papers of Hans Beckey from the University of Bonn. And what did I learn about field ionization from him, from his work? There was no hydrogen scrambling. I hate the word ‘scrambling.’

GRAYSON: [laughter]

NIBBERING: Because it is as if this is not rational, what is going on there. I mean, it turns all the organic chemists [off]. So I prefer to use the word ‘randomization.’ It’s a little bit friendlier. That’s the same effect, of course. But that brought me into field ionization and also with field ionization you could get molecular ions of compounds which were not seen upon electron ionization.

GRAYSON: Right, exactly.

NIBBERING: [. . .] But it took . . . well how many years did it [take]? First, the installment of—the installation of—the machine took a lot of time but before we got the field ionization source in our lab, that was in ’74, not earlier. And that’s another story, perhaps, which is of interest. The beam was very unstable, in the beginning, of the Varian MAT machine. [. . .] I’ve always had, with all the companies, by the way—with AEI, and VG, and MAT, Varian MAT—always a very good relationship with the people there; really, believe me, no problem. But they changed, of course, the boxes, the electronics, and see whether it was an electronic instability, and nothing developed. Then Karl Heinz Maurer from MAT Bremen company [Varian MAT GmbH] came over to Amsterdam. Well he was a very experienced man, because we would like to work with the instrument. And he tried everything, and then it turned out that the beam became very stable.

GRAYSON: Let’s take a little time out here.

NIBBERING: Well I have to finish this. [. . .] So the instability of the ion beam, then he found out by working at night—until a quarter past one—and then the beam was very stable. And then he worked on, checked everything, and at a quarter past five, the beam became very unstable. And it turned out to be the trams in Amsterdam. [. . .] Because the trams are running on—trams,

you know, street cars. These are running on DC, direct current. And the only other place is Sao Paolo, [Brazil], where they also have direct current.

GRAYSON: That's pretty unusual.

NIBBERING: [Yes], it's unusual. And they did measure, of course, they checked before installation of that instrument in the cellar down in the lab where the environment was okay. But they measured the wrong frequency, I think, or something like that. Then they came up also with a solution. They sent over a certain man I think his name was Dr. König—like “king”—he was a very silent scientist that working, doing measurements. And they went back, and they simulated the street car by putting wires in the gutter of the company to . . . well <T: 130 min> simulate the magnetic fields variations. Of course that was the cause, which we didn't see with the AEI MS 9, because that beam was deflected in the vertical direction so that it doesn't matter if you have that.

And then he said we should make a coil of 740 meter copper wire in a wooden frame where the frame had to be made on-site and then at a certain point in the center had to be at the entrance to the electric sector, and then a pick-up coil at the ceiling that sensed the variation of a magnetic field and compensated for that, and then we have a very stable ion beam because the earth magnetic field is two milligauss. And they're stable. But this was compensated immediately and . . . they guaranteed this is also Germanic you guarantee a resolving power within 10 percent valid definition of seventy thousand but it was then ninety thousand.

GRAYSON: So they made these measurements.

NIBBERING: [They] measurements in our lab. And then went back to Bremen and simulated the tram by putting a wire and then came with the solution you should have a coil of seven [hundred copper wire in a wooden frame].

GRAYSON: This thing hanging in a . . .

NIBBERING: Hanging, it is in the slides if you look later on then you can find it. You can see it and I mentioned that those were in the *Mass Spectrometry Review* paper.

GRAYSON: So the one coil picks up?

NIBBERING: Picks up the variation, physical and compensating by [an electronic current]

through the wire through the coil. Because we had heard about the story in Klaus Biemann's lab where they also had these electrical problems that you had to work with metal to avoid the magnetic field lines. I thought, "Oh, oh, oh, that will become very expensive." It was a nice solution.

GRAYSON: [Yes], that's crazy.

NIBBERING: [Yes].

GRAYSON: That guy must be a genius.

NIBBERING: [Yes], was a genius, yes.

GRAYSON: [laughter]

NIBBERING: Herr König.

GRAYSON: Herr? It was . . .

NIBBERING: König, [yes]. [. . .] I remembered the name König.

GRAYSON: That's all they . . . okay.

NIBBERING: That's all that I know.

GRAYSON: Pretty neat.

NIBBERING: It's neat.

GRAYSON: That's amazing.

NIBBERING: It's amazing, yes.

GRAYSON: It's really strange, well I guess he knew his business [laughter]

NIBBERING: [Yes].

GRAYSON: So this was with the . . . was it the 741? No, it was with the ICR machine where the . . . ?

NIBBERING: No, this was the Varian MAT-711.

GRAYSON: It *was* with the 711?

NIBBERING: The double-focusing mass spectrometer with a Mattauch-Herzog geometry.

GRAYSON: Okay.

NIBBERING: The drift cell ICR, that we had also electropollution. But that was another problem. There you work with oscillators.

GRAYSON: All right, okay.

NIBBERING: So, there, the pollution was such that you could not get good signals out of it but that has also been solved.

GRAYSON: [. . .] All right, so you were able to get the money to buy this equipment . . .

NIBBERING: [Yes].

GRAYSON: . . . and this is something that's going on through your whole career though. I mean this is . . .

NIBBERING: Because the AEI MS 902, the Varian MAT-711, the drift cell ICR was bought . . .

GRAYSON: Drift cell? I'm sorry the . . .

NIBBERING: That was the Syrotron [. . .] Varian Syrotron.

GRAYSON: Varian, okay.

NIBBERING: Varian Syrotron, drift cell ICR.

GRAYSON: They call it drift . . .

NIBBERING: Drift cell, drift the ions under the influence of electrical and magnetic field.

GRAYSON: Drift cell ions.

NIBBERING: [Yes], because the . . . well we modified, also, a lot ourselves on these machines. So let me try to tell it in an organized way. The drift cell had three sections: an ionization region, an analyzer region, and a detection region. They were the three-section cells. So it was sold by Varian—the Varian company in California. We made a four-section cell. That means an ionization region, then an ion-molecule reaction region, then an analyzing region, and then a detection region.

GRAYSON: Okay.

NIBBERING: So that was the first modification we did ourselves, to improve for ion-molecule reactions. Then, of course, the pumping system, as I mentioned. Instead of having an ion getter pump, also have a mercury pump for the <T: 135 min> inlet systems, et cetera, to keep the vacuum as good as possible. Also we worked with a direct insertion probe. [. . .] But I think we were one of the first who had a direct insertion probe . . .

GRAYSON: Okay.

NIBBERING: . . . to measure in a drift cell ICR. I can assure you that—Mike—that these are difficult experiments. Because to find out whether a reaction was occurring, if it is exothermic, then you had a negative ion response, because what you did, you played with the cyclotron frequency of the ion. And if you accelerated, then there was more product, but the signal had a sign. Charge transfer was always positive. Exothermic was negative. So with the direct insertion probe the pressure was so unstable, we needed to know whether the reaction was going, yes or no. So we had to have . . . to see a so-called double-resonance signal [. . .]. Was the double-resonance signal ending up in a negative response or was it positive? Positive for charge transfer, negative for a real, let's say, proton transfer.

GRAYSON: Okay.

NIBBERING: And we did that experiment with Joe [Joachim] Memel from the Polytechnic in London [North East London Polytechnic]. He was for one month in Amsterdam, and then after one month's struggling all the time, watching, I said to Joachim, in the end—that is also in the review paper—"Joe, it is an exothermic reaction, the signal is negative." But since that time we didn't use any more the direct insertion probe.

By the way, that instrument was also not used for analytical purpose.

GRAYSON: Okay, sure.

NIBBERING: Only research. But for that particular case it was important to see whether the reaction we thought was going was really going. But that is an intermission statement. I don't know whether you know about distonic ions.

GRAYSON: Only that I've heard of them from Michael [Gross].

NIBBERING: Now distonic ions . . . this is an ion-molecule reaction where a distinction is made between a distonic ion and a normal ion. Via ion-molecule reaction.

GRAYSON: Okay.

NIBBERING: Michael has also shown that in the beginning of his career.¹⁶ He had a cyclopropane ring within an amino group and that turned out to be a distonic ion in the end. But that is, for scientific purposes, interesting, then.

GRAYSON: Obviously you can't run all this equipment, so you have students running it?

NIBBERING: Students and technicians.

GRAYSON: Technicians.

NIBBERING: [Yes].

GRAYSON: So you were able to . . .

NIBBERING: And, later on, PhD students.

GRAYSON: Okay, but you were able to hire technicians to . . .

NIBBERING: No, in my group we had Frans [A.] Pinkse. We called it a lab assistant. But Frans was a lab assistant, we call it in the Netherlands, a chemical analyst.

GRAYSON: Oh, okay.

NIBBERING: But then I think that term is not used in the United States. It's a lab technician. But Frans started as a lab technician in chemistry but had interest in electronics. Therefore I managed to get them in my group not to do all the time measurements with the machines, but also to work on electronics, designing things with the instruments of the workshop. And that enabled us, also, together in the workshop to modify our instruments. And also with the help of Jim [J. H. J.] Dawson, who I will mention later. But Jim was a postdoc in my group based on a NATO [North Atlantic Treaty Organization] grant in the beginning, coming from Keith

¹⁶ Michael L. Gross and F. W. McLafferty, "Identification of $C_3H_6^+$ Structural Isomers by Ion Cyclotron Resonance Spectroscopy," *Journal of the American Chemical Society* 93 (1971): 1267–1268.

Jennings' group. And so that helped to do things ourselves. So for example, to list a few things: on the MS902 we made ourselves a so-called beta slit to have more selection of the ion beam, et cetera. Then on the Varian MAT field ionization we developed a field emission control unit, ion emission control unit, to get stable emission of ions during the field ionization.

[. . .] And then, of course, in the end we made the Fourier transform ICR. But it isn't—why that happened is, again, another story. Yes, <T: 140 min> PhD students did run the double-focusing instruments also for their research but also—and it was allowed by Professor Huisman and Professor de Boer because Frans Pinkse went to designing and making electronic things.

GRAYSON: [. . .] Okay. And then there was this Jim?

NIBBERING: Jim Dawson.

GRAYSON: [Yes].

NIBBERING: Jim Dawson.

GRAYSON: [. . .] Ah, Dawson. Dawson.

NIBBERING: Also if you have problems, if you look in the *Mass Spectrometry Review* article, then you will find—or in the publication list you will find the names. And then we have Mr. [W. J.] Rooselaar. He is only mentioned in the acknowledgements. He was an older man. [. . .]

GRAYSON: Okay.

NIBBERING: He came from industry and knew Henk Hofman, his wife, and he was fired, and then he was hired at a university, so he entered mass spectrometry when he was forty-five or forty-six. But scientifically, no, he was not participating in the papers. He didn't want also but for example papers with the lab technicians I put simply the names on it because my attitude was always they have contributed a lot. You will say, perhaps, they should be able to defend everything but we are—I think if somebody has made a very [worthy] contribution, why not?

GRAYSON: Sure. That's fair.

NIBBERING: That's fair, exactly. That's the right word, to be fair. And some of them have very good training. And believe me the lab technicians are very well-trained, and another one will come later on, I think, in the names.

GRAYSON: Very good. The whole focus was to do these applications in terms of people who are submitting samples for the analysis.

NIBBERING: [Yes].

GRAYSON: And this would be an opportunity for the graduate students to develop their skills with the instrument and the interpretation.

NIBBERING: And they used, of course, the instruments for their own PhD.

GRAYSON: Right, and so did you end up having . . . I mean every mass spec lab I know of has had those wonderful accidents where, you know, the vacuum gets busted, broken.

NIBBERING: Oh [yes].

GRAYSON: [laughter]

NIBBERING: Oh, we had an accident with a direct insertion probe on the Varian MAT-711. These probes are very expensive, something like ten thousand guilders, so you have to slide them in. And then there was a valve, of course, that locked the vacuum and then when the direct insertion probe was slipped in, at a certain point, you had to open the valve and slide it further. So the vacuum was not attached. Then when you have to put in another sample, then you have to withdraw the direct insertion probe, close the valve, and then you can get out the direct insertion probe. Well, what happened, now, the probe was still there and the person in question was a postdoc. He turned the valve, whereas the direct insertion probe was still there. So the direct insertion probe was really damaged. And that was not easily [repaired] because that had, also, these wires to heat it and cooling, et cetera. We were not so happy with that, huh?

GRAYSON: [laughter] Right. And then there's also the vacuum—loss of vacuum—unexpectedly.

NIBBERING: [Yes]. In that case the direct insertion probe was there, but it destroyed the direct insertion probe and indeed the vacuum. But then of course I get it as soon as possible further on and close it further. But I must say it had an ion getter pump in the end, the Varian MAT-711 instrument, and the getter pump has never been replaced until they threw away the instrument. And that was in the nineties. But, Mike, I really—the Varian MAT-711 was an extremely well-designed instrument for analytical purposes. But there is also a problem to modify [things yourself] . . . well we did it. But for example, the software, also, because it was analytically—later on even more—made that you could not easily change it anymore. So they guaranteed a very stable <T: 145 min> working horse.

For your information, that is, of course, playing with the instruments. As soon as we started to do field ionization, then I would like to do field ionization kinetics, where you could see the decomposition of ions from picoseconds to microseconds in a time-resolved way. You know electron ionization, there you have ions which stay in the ion source for a microsecond—now the formation times are 10^{-12} , 10^{-13} , something like that. So, many reactions can occur for highly energized ions and lower energized ions. If you take a picture with a camera you do this all the time. It is very diffuse. But then with field ionization kinetics—and it was done by Al Burlingame and Peter [J.] Derrick already, and in Beckey's group in Bonn, but we got the source in '74. So field ionization kinetics had just been published.¹⁷ Field desorption we could not get earlier than 1974 and the field desorption was already there.

But, with regard to the field ionization kinetics, first we had to develop a program to do a high voltage scan, and from there you could calculate the time where the ions had decomposed between the electrodes. And so Christ Kort managed to write a completely new operating system for the Varian MAT-711. And I can say to you the guest scientists like John [H.] Bowie had been in our group. He was surprised to see that. I mean, we did analytical applications, but the next day we did pure research, and then an FIK [field ionization kinetics] scan. Immediately there was the phenomenological before we made that program, Jan van der Greef, who did field ionization kinetics by hand, that took three months to process the data. And then it turned out that he said, "Oh, I should have better defined my molecular ion conditions." And that was easy when the program was made.

But also—that was the field ionization kinetics. Field desorption is another story because tunneling of electrons from the molecule to the emitter, you should not have high pressure. But now you go to field desorption where you put a sample on a tungsten wire, activated tungsten wire—because that was used both in field ionization and field desorption—and then you apply a voltage of 8 kilovolt difference. And you have the emitter loaded with your sample, 1.5 millimeter from a counter electrode with a small hole in it. And then manually you have to put some current through it to heat the wire and then ions are coming off. But if it is heated too

¹⁷ H. D. Beckey, K. Levsen, and Peter J. Derrick. "A standard form for the presentation of field ionization kinetics data." *Organic Mass Spectrometry* 11, no. 8 (1976): 835-837.

much, suddenly you have an explosion of ions that is a discharge and the wire breaks, of course a 10-micrometer tungsten wire is very fragile.

GRAYSON: [Yes].

NIBBERING: So in the beginning when Frans did it—Frans Pinkse—the wires were broken because he could not manage that. I said, “Frans, stop,” because these wires were about three hundred guilders. So, I said, “Stop, stop, stop, stop, we cannot do that.”

So then—but I had been in Bonn also many times with a group that we went to Bonn. To Beckey, but also Karsten Levsen, and Hans-Rolf Schulten, and Franz [W.] Röllgen. I had a paper with Hans Schulten on field desorption.¹⁸ And he used, already, emission control so that you could control the ion current coming from the emitter that was for operating the system, the mass spectrometer much better, of course.

Now Jim was with us, Frans was with us. As I said, I took also the lab technicians with me on these trips to visit labs not . . .

GRAYSON: Okay.

NIBBERING: . . . also to conferences but not so many times Frans didn’t want that and it was also not custom in our faculty of chemistry that lab technicians went to conferences.

GRAYSON: Sure.

NIBBERING: When I made a visit in Bonn, that was no problem. We took the people with us. I drove my car. Then on the way back I remember very well the <T: 150 min> discussions in the car with Jim Dawson, and with Frans Pinkse, and then Carla [B.] Theissling was a PhD student who went there for doing collisional activation studies. [. . .] Then on our way back to the Netherlands, then the design for a much better field emission control unit was discussed—and made later on. And that is a lot, to do field desorption. So you see the modifications, we were not afraid to do that. But always, in a way—especially for the instruments—if it was your own research, then you could do everything what you wanted, like drift cell ICR.

¹⁸ H-R Schulten and N. M. M. Nibbering, “An emission-controlled field desorption and electron impact spectrometry study of some N-substituted propane and butane sultams,” *Biological Mass Spectrometry* 4 (1977): 55-61.

GRAYSON: Sure.

NIBBERING: But with the AEI MS9 and the Varian MAT-711 machines, you could not do *risky* things because if you would destroy the instrument, then the organic chemist would not have their analysis, and then the hell would break out.

GRAYSON: [laughter] Well, what do you think? Let's say we take a break?

NIBBERING: [Yes].

GRAYSON: Okay.

NIBBERING: Okay.

GRAYSON: Very good. [. . .]

[END OF AUDIO, FILE 1.1]

[END OF INTERVIEW]

INTERVIEWEE: Nico M. Nibbering

INTERVIEWER: Michael A. Grayson

LOCATION: Hilton Hotel
Minneapolis, Minnesota

DATE: 8 June 2013

GRAYSON: I'm going to start again by saying that this is the eighth of June, now, and we're continuing the discussion that I'm having with Professor Nibbering, with regard to his career, that we interrupted yesterday for a break. Do you recall exactly what we were talking about at the time? We had kind of gotten into your laboratory, after [. . .] the point where you had taken the job as director of the mass spec facility. We talked about instrumentation that you had purchased and the fact that you had gotten involved in ICR. What other things did you want to pick up on in that particular discussion?

NIBBERING: I would like to mention that we discussed, also, the field ionization.

GRAYSON: Ah, yes.

NIBBERING: Field desorption—that was the end—on the Varian MAT-711 instrument. And that we developed a so-called electron emission control unit to control the ion emission from the emitter to the counter electrode in the case of field desorption. Then that helped to handle the fragile emitters, which are 10 micrometer tungsten wires. They don't break, then, so easily. You could really control it in a way that you could have stable ion emission current for hours, even. And although that was later in time, but it had to do with the drift cell ICR work which I mentioned before, that we worked on negative ions interacting with neutral molecules. We had interest in negative ions, and that also, well, gave the motivation to do negative ion field ionization and negative ion field desorption. And especially the negative ion field ionization, that is a very hard thing to do. Because instead of tunneling an electron from a neutral molecule to the emitter—then you get a positive ion—in this case you have to tunnel an electron from the emitter to the molecule.

GRAYSON: Okay.

NIBBERING: And emission of electrons from, well, a tungsten wire . . . it can give you an enormous amount of electron emission but it has nothing to do with tunneling to a molecule.

You have to be very careful that you don't get something like an electron ionization of the molecule because of a loss of electrons. So what we did is, we lowered the potential difference between the emitter and the counter electrode. We increased the distance for that, in addition to that. And then we checked with tetracyanoethylene, which is a molecule which has a reasonably high electron affinity. And then we made the molecular radical anion of tetracyanoethylene. And then by varying the pressure of the tetracyanoethylene, and then looking at the intensity of the molecular anion, that behaved like it was proportional to the concentration of the neutrals in the gas phase.

GRAYSON: Okay.

NIBBERING: Also, if you have no molecule there, there was, then, also not an electron emission, you see? So that way, we really were sure that we are dealing with a tunneling effect.

GRAYSON: When you had these tungsten emitters did you have to grow . . .

NIBBERING: We did design ourselves a device to activate these tungsten wires ourselves in an atmosphere of benzonitrile.

GRAYSON: Okay, so that was a given part of the experiment, was getting the . . .

NIBBERING: <T: 05 min> Well we had made that before already, yes, for the positive ions because, as I told earlier, the tungsten wires were too expensive for us, and therefore you had to make this device. Or you could buy them. But then, of course, that required a lot of money. If you buy them officially from the company that was very high in price but you had, also, small companies who made these wires but we've decided to do it ourselves.

GRAYSON: Was that a very difficult problem, to grow the emitters?

NIBBERING: No. No, not really. I mean, you have to find out the conditions, of course, but when you have found that out, then it is a standard procedure.

GRAYSON: Okay.

NIBBERING: Also, because I have talked now about the field ionization of making negative

ions in the gas phase, but that also turned very beneficial to do negative ion field desorption, which had not been done before by other people. But then, you didn't need, in the end, to have activated wires. You could also work with smooth wires.

GRAYSON: Oh, really?

NIBBERING: [Yes], because if you put on, let's say, a salt, then the negative ions from that salt could be desorbed from the wire. We also learned, of course—we did compounds like arginine, sugars. Of course, if you have a sample which is heavily contaminated with salts, that is not so good for the emission of ions, because you get something like a splintering. Suddenly the ions desorbed, the field emission control unit had, then, problems to stabilize. But what we did, we diluted—most of the time, in that case, when there was too much salt—with polyethylene glycol. [. . .] Something like that, a polymer. To mask a little bit of the high concentration of the salts. And then it worked.

So we have had a very good experience with field desorption. Contrary to the common feeling about it that had especially to do with the fragile character of the wires. But with the field emission control unit, that was an excellent device to get that in the hands of people who should have been capable to work with instruments, but didn't require so-called *Fingerspitzengefühl*. That is the German word for it, and that was not required.

And the emission of the ions, as I said before, you could control the saturated, you had a stable ion current for hours. Because you could control the number of ions coming off the emitter. And that was all processed in a computer, so you accumulated the scans. You did a scan, and then accumulate it all the time, and then you had the result. Now, that was a very good thing.

GRAYSON: The idea that you could have a stable ion current from that was pretty impressive.

NIBBERING: [Yes].

GRAYSON: That was an excellent And I know that most people considered the field ionization desorption techniques to be really challenging. And I think they probably were, compared to what you normally do, but once you meet the challenge by using your proper skills and knowledge, then you can obviously do quite a bit with it.

NIBBERING: By the way, [Charles Crawford] Sweeley, he made, also, an emission control unit. We didn't know that, of course, at that time, but I've seen later on the publication.¹⁹

GRAYSON: Sure.

NIBBERING: And he had the same experience.

GRAYSON: So if you do it right, then it works.

NIBBERING: He worked in the positive ions. For us, the new thing was that we not only could do positive ions but also negative ions. And I must say we cooperated with Franz Röllgen, from the Bonn University, about that, because, in the beginning, especially negative ion field ionization, that was critical to accept that because it's that electron emission which then is attached to the molecule is a pure, pure field ionization. But he was convinced by our experiments, and we got cooperation further in the negative ions, especially the field desorption. But I mentioned before that we had a good relationship with the people at the University of Bonn. <T: 10 min> I mentioned this because then it is better to understand about the Varian MAT machine field ionization, field desorption presented as one piece—independent of the time things happened.

GRAYSON: [Yes], sure. So you did this on the . . .

NIBBERING: On the Varian MAT machine.

GRAYSON: Which is a high-resolving power instrument?

NIBBERING: [Yes].

GRAYSON: Okay. And you did get accurate mass data and so on?

¹⁹ Maine, J.W., et al., "Emitter current programmer for field desorption mass spectrometry," *Analytical Chemistry*, 1976. 48(2): p. 427-429.

NIBBERING: [Yes].

GRAYSON: Okay.

NIBBERING: Sure.

GRAYSON: That's good.

NIBBERING: And even . . . we could heat, of course, the emitter a little bit so that you had also thermal-induced fragmentation of the ions.

GRAYSON: Ah.

NIBBERING: So for structural elucidation, or it gets structural information. I must say that organometallics, for example, we run them both in a positive ion mode and in the negative ion mode. You could characterize the organometallic compound in that way, because most of the time field desorption doesn't show fragmentation. You have a good idea about molecular weight, but you have no structural information. But I am remembering a manganese cobalt complex. In the positive ion mode, the whole complex was ionized intact, and when you turned over to the negative ion, then you had the cobalt part of it.

GRAYSON: You were interested in doing a negative ion work so that you could work with compounds that were not amenable to positive ion analysis? Or just because you wanted to do negative ions?

NIBBERING: [Yes]. Exactly, that is the idea. If you have a neutral compound and it can add a negative ion, like an OH⁻ ion, then you could, of course, do field desorption. So you could play in that way with it. Masses . . . with regard to molecular weights, how high they could be . . . well we have run between four thousand and five thousand daltons. I think that Hans Schulten had the same experience. If you go to higher masses, [T.] Matsuo from Japan, he presented at the [1979] International Mass Spectrometry Conference in Oslo, [Norway], and it was in a polystyrene molecule, as far as I remember. And he showed, then, that he could take ten thousand daltons, but that was really the limit. Unless—we did it later with a JEOL 4-sector instrument, but that is even further in time, so it was later in my career. If you had polymers you could add, let's say, charged alkali ions, like sodium, potassium, these kinds of species. You could then make multiply charged. So we have had examples, more or less at the end of my

career, so in the mid-nineties, where we had seven alkali ions attached to one polymer. And so we have a seven-plus charged state. And that means that you can then detect high masses because of the highly-charged. It resembles like what the people doing nowadays in electrospray ionization. That has never been exploited further, because I think, what you also said, the field desorption technique was regarded as very challenging.

GRAYSON: So you had done this, you were aware of the multiply-charging possibility. Did you use that information to then create the pseudo-molecular ion from that?

NIBBERING: Yes.

GRAYSON: So you were able to . . . okay, so this is basically . . . you did some of the things that the people in the electrospray community were doing—did later?

NIBBERING: [Yes].

GRAYSON: You were doing them earlier with these . . .

NIBBERING: Earlier it . . . it was in the nineties, so I think we have a publication around '94-95.²⁰ A record of communications, and electrospray was already used. But, for us that was to play around. But that was not done on the Varian MAT-711 instrument. That was done on a four-sector JEOL machine.

GRAYSON: JEOL?

NIBBERING: [Yes], JEOL.

GRAYSON: Okay.

²⁰ P.O. Staneke and N.M.M. Nibbering, "Matrix-assisted laser desorption ionization and electrospray ionization combined with Fourier transform ion cyclotron resonance mass spectrometry. *Spectroscopy* 13, 145-150 (1996/1997).

NIBBERING: And I think it is [JEOL] JMS SX 2A, or something like that. <T: 15 min> Well, I have to look in the review article which I wrote so not to make errors in the numbers. But it was the four-sector machine which was installed in '91 in our group that was during the year that the International Mass Spectrometry Conference was held in Amsterdam. And I managed to get a grant before the meeting to buy that instrument, and it was then installed in '91 in the lab. But that is much later in time of course.

GRAYSON: Sure. So where do you want to go from there? We've got the . . .

NIBBERING: Now I would like to switch the time. Drift cell ICR, we started that and you know from the discussion in the interview that that was induced by the trip to the United States in '69. But then, having the Varian MAT-711 installed and working with that, then the reverse geometry mass spectrometry came up, where you could have in a double-focusing instrument first selection of ions by the magnet and then do a collision, and then analyze the mass selected ion beam, the fragments of it by scanning the electric sector. So the reverse geometry instrument was for that reason a very nice instrument to do ion chemistry. Because of the selection of mass.

So, I applied for such an instrument at the—I call it the, now for this moment—the [Netherlands Organization for Scientific Research]. They said, because it was a high amount of money for these instruments, “Do you know a place where you could do this collisional activation experiments on mass selected beams?”

And I said, “[Yes], in the lab of Fred McLafferty.”

So they said, “Well, you, can get a grant for that and go to Fred McLafferty as a visiting scientist and do experiments there.” So, that induced, of course, my trip in 1974 to the lab of Fred McLafferty in Ithaca, New York State. And I stayed there, I worked there for, I think, two to three months. And we agreed of course in correspondence on what kind of problems we would like to study. One of them was the phenonium ion—that is in the benzene ring with a so-called cyclopropane unit on it, so the two CH₂ groups are attached to one carbon atom of the benzene ring. So that is the phenonium ion. [. . .] Phenonium ion structure.

GRAYSON: So, that's a benzene ring with these two CH₂ methylene groups?

NIBBERING: CH₂ groups, yes.

GRAYSON: CH₂?

NIBBERING: It is actually an ethylene attached to one of the carbon atoms of the benzene ring.

GRAYSON: Ah, okay.

NIBBERING: And that ion was in solution chemistry, but gave a lot of debate between [Herbert C.] Brown and [Saul] Winstein. One of them thought it was in the phenonium ion whereas the others said, “No, no, it is like a windscreen wiper.” [. . .] As an organic chemist that was really interesting to see what a mass spectrometer could show. I took also the labeled compounds with me, and then arrived in the lab of Fred, and then we worked on that together with Takao Nishishita from Japan. He was postdoc’ing there and Chris [Christian C.] van de Sande from Belgium.

GRAYSON: You published a paper with those people in it?

NIBBERING: [Yes], and with Fred of course.

GRAYSON: Okay. I’ll just check the literature for . . .

NIBBERING: You can find the literature because I have put a reference in the *Mass Spectrometry Review* article which I wrote.

GRAYSON: Very good.

NIBBERING: I had a good time in Fred’s lab. Well, Takao Nishishita and Chris and I were called by him the three musketeers. [laughter] And, you know, <T: 20 min> in the end three papers came out of that visit.²¹ It was very successful. Well, we worked from half past eight in the morning until late at night and did that every day. I didn’t mind because I was very, well,

²¹ N.M.M. Nibbering, T. Nishishita, C.C. van de Sande and F.W. McLafferty, “Long-lived β -phenylethyl and ethylenebenzenium cations in the gas-phase.” *Journal of the American Chemical Society* 96 (1974): 5668-5669 ; N.M.M. Nibbering, C.C. van de Sande, T. Nishishita and F.W. McLafferty, “Collisional activation spectra of the [C₉H₁₁O]⁺ ion from 2-methyl-2-phenylpropane-1,3-diol,” *Organic Mass Spectrometry* 9 (1974): 1059-1061; Claus Köppel, C.C. Van de Sande, N.M.M. Nibbering, Takao Nishishita and F.W. McLafferty, “Thirteen stable isomers of gaseous C₈H₉⁺ cations.” *Journal of the American Chemical Society* 99 (1977): 2883-2888.

eager to get the results because I would like to show the people in the Netherlands that this was a very useful method for gas-phase ion chemistry.

GRAYSON: So this was kind of like a proof of principle trip to see if you could . . .

NIBBERING: So: to get money for a new reverse geometry instrument. But then also, in 1974, there was then the twenty-second ASMS [American Society for Mass Spectrometry] meeting in Philadelphia, [Pennsylvania]. Fred went there with his group and, of course, I had joined the group there. I attended then that meeting. There are two important things, and again you see how important to travel and to meet people. First I met Michael Gross there for the first time.

GRAYSON: Oh boy. [laughter]

NIBBERING: And in some way it immediately clicked between us. We became very, very good friends. I said yesterday to Michael, “Wouldn’t it be nice if we were to live closer together?” Then you could visit each other a little bit more.

GRAYSON: [Yes].

NIBBERING: Since then we have had very good contacts. Michael has been in my home, and we have discussed ion chemistry from—starting in the evening until 4:30 in the morning. And that I said, “Now the sun has come up, it’s better now to go to bed so that we don’t get problems with our wives, et cetera.” [laughter]

GRAYSON: [laughter]

NIBBERING: But it was another thing, then, which was very important and that is during that conference Mel [Melvin B.] Comisarow presented the paper on the first experiment done to show Fourier transform ion cyclotron resonance [FT-ICR]. Fourier transformation on ICR and he showed a molecular ion of methane. He did that experiment in 13 December 1973, [. . .] together with Alan [G.] Marshall at the university—from Vancouver—in British Columbia. [. . .] British Columbia I think, yes.

Now, listening to that lecture and doing, myself, drift cell ICR, you can imagine that I was really excited about this method. And I think that Michael, he was also doing drift cell ICR,

so he has perhaps had the same idea about it. But the audience was skeptical. Because they asked Mel Comisarow, “Can you do it to get a broad mass range?” and that was a problem.

So, I remember that Mel said, at that time, “In principle, of course, that’s possible. But I need a very large grant, so much so that it’s almost a whole National Science Foundation budget. And my colleagues are of course very nice but not so nice that they don’t get the money from the National Science Foundation.” But the rest of the audience, nice, but skeptical: “Is that useful?”

GRAYSON: [Yes].

NIBBERING: You can understand that, hey? After I returned to the Netherlands again—from working in the lab of Fred McLafferty, attending the ASMS, meeting Michael—then, as soon as I came back in the lab I told, of course, the people what I heard about the FT-ICR. And my question was, could we make such an instrument? At that time, Jim Dawson—mentioned before—he was postdoc’ing with me. He was from the group of Keith Jennings, had received his PhD there at the University of Warwick, and then joined my group. Jim was a wizard in **<T: 25 min>** electronics. He was also a registered accountant, was a physical chemist. He came from a very good family. He was the only child of . . . was also a wealthy family, so he didn’t have to work for us, but he was on the basis of a NATO grant in my group. And so Jim said, no way. Now okay, but we had also students from electric technical high school from Amsterdam in our group, simply to practice. With Frans Pinkse, mentioned before, to build things electronically. To change things at instruments which we were operating. And Frans said to me that the microelectronics was developing very fast.

GRAYSON: Okay.

NIBBERING: And also the computer technology was developing very fast. So I repeated my question many times about “Can we build an FT-ICR?” and at the end of ’78, Jim Dawson said, “Perhaps.”

GRAYSON: From “no way” to “perhaps”?

NIBBERING: And when he said that and I said, “Jim, then we will do it.” And I asked for a grant from the [Netherlands Organization for Scientific Research]. And so, I got a grant for him and so we start to build the FT-ICR with all the designing of electronics, et cetera, on the first of April in 1979. The following people were involved: It was Jim Dawson, Frans Pinkse, Chris Kort, whom I mentioned before [. . .] Andre [J.] Noest. Andre Noest is a new name, he was a Master Degree student and a PhD student in my group. [. . .] He came from the the Vrije

Universiteit and did his PhD with me. And he was heavily interested in computers. So the communication with Christ Kort, that helped also, of course. Now then the instrument workshop, so the cell was designed, et cetera. And then it was planned in such a way, Mike, that the other PhD students, they could use, all the time, that drift cell instrument. I remember that Jim said in November '79 [. . .] "We are now at a point, do you want to go back, if you change the instrument to an FT-ICR, to a drift cell ICR?"

But I said to Jim, "How sure are you that the project will be successful?" I'm not an electronic man. I was interested, but I could not do that kind of work.

He said, "Well I don't know."

"Well, Jim, then we should be able to get back to the old situation," because otherwise the other PhD students could not do their work for their thesis. Okay, so that was decided, and then in three weeks' time the instrument was converted from drift cell to FT-ICR. But I would like to mention also Jim made the radio frequency synthesizer himself.

GRAYSON: Okay, oh wow. [laughter]

NIBBERING: [Yes], wow, wow. This was really—he was a very strong person mentally but he almost had a nervous breakdown. So we also found each other at night. And then Jim said, "It cannot work!" And then from the discussion, "Okay, [yes]." So that helped. But there was also in discussion in the group that Jim was a hardware man and so he said it should be hardware controlled. But Andre Noest, he was more the computer-oriented man, and he said it should be software controlled. And the decision had to be made, and at that time he said, "Okay, then hardware controlled." Because our concern was if you did an FT-ICR scan, chirp, <T: 30 min> then you looked at the signal, and then you had to accumulate the signals to get a reasonable signal-to-noise ratio. And Jim was convinced that by hardware was no problem to do that. Whereas Andre said it can also be done by software. But you realize also that the computer was a [DEC, Digital Equipment Corporation] MINC-11 with a 32K memory, MINC-11.

GRAYSON: Wow.

NIBBERING: So it was very small.

GRAYSON: Thirty-two K?

NIBBERING: [Yes]. And we had then, of course, floppy discs. So that was the reason why we said, okay, we do it in a hardware control.

GRAYSON: [Yes].

NIBBERING: If you look back then, the software controlled approach is nowadays

GRAYSON: Oh [yes]. Everything is software controlled.

NIBBERING: Oh [yes]. We are talking about, hey, the first spectrum came out the second of April 1980. And so, it was exactly one year plus one day that we had the first spectrum from acetone. And that instrument has been very successful to do basic ion-molecule chemistry. Both positive ions and negative ions.

GRAYSON: Great.

NIBBERING: I must say many PhD studies came out of it, but also cooperation internationally that people came to Amsterdam to do experiments with that kind of instrument. But between that period, from coming to the idea of making an FT-ICR since I returned from the lab of Fred McLafferty. So, that was successful. I was still thinking about the double-focusing instrument with the reverse geometry describer because that was the reason why I went to Fred. And I had written a proposal. I think thirty-five projects in detail and I think I still have it at home.
[laughter]

GRAYSON: So this is for the reverse geometry

NIBBERING: Reverse geometry instrument to have a project for it.

[END OF AUDIO, FILE 2.1]

GRAYSON: [. . .] Do you remember where we were in our discussion?

NIBBERING: Yes, I mentioned, of course, that I had written the proposal to obtain a reverse geometry mass spectrometer, the thirty-five projects, and then upon return from Fred's lab . . . FT-ICR discussed construction of the home-built. But now coming back to the reverse geometry instrument. That grant was not awarded by the Netherlands Organization for [Scientific]

Research—I mean the Dutch National Science Foundation—because Professor [Geo] Dijkstra who was professor of analytical chemistry at the University of Utrecht, he managed to get a grant from his own university to buy such an instrument. And so, the Netherlands Organization for [Scientific] Research thought they will try to get time for me to do measurements on that instrument when it was installed. But they managed not to get attached to their instrument.

What then happened, of course, is that I tried to get collisional activation [. . .] experiments done with colleagues outside the Netherlands. So, with the University of Bonn, with Professor [J. H.] Beynon, with Professor Jennings.²² And so that induced also a lot of international cooperation in that way. And that was—for me it was a negative result that I didn't get the instrument, but on the other end there was a positive side on it so that we could cooperate more with colleagues outside the Netherlands.

Then, in the end, I received then upon . . . well, again submitting a proposal, I think it was in 1980, then I managed to get the money for a reverse geometry instrument at the end of 1980, and then the instrument was installed in 1982. And that was a VG Micromass ZAB 2HF mass spectrometer. [. . .] With, of course, a new data system. [Fig. 6] So, everything included, so then we could do ourselves . . . well the mass selected collisional activation work.



Figure 6. Tube unit from the VG Micromass ZAB 2HF double focusing instrument

²² John H. Beynon, interview by Michael A. Grayson at Swansea, Wales, United Kingdom, 22 April 2008 (Philadelphia: Chemical Heritage Foundation, Transcript #420).

Meanwhile I had been in 1980 in the University of Colorado in Boulder with Chuck DePuy, where I presented a summer course consisting of ten research lectures there. So I was, again, back in the United States.

But then, another thing I would like to mention is, when I received the grant to buy a reverse geometry mass spectrometer then Professor Los, the director of the FOM-Institute in Amsterdam—I had a very good relationship with a physicist there. He invited me to join that institute. [. . .] Joop Los, he was the successor of Jaap Kistemaker. Jaap Kistemaker was the first director of the FOM Institute, AMOLF, in literature [. . .]which stands for Atomic Molecular Physics Institute.²³ But then I said to Joop Los, “That’s very nice that you invite me but, I just got a grant to buy that reverse geometry mass spectrometer, which took me eight years.” And I cannot say, “Well, I cannot accept your invitation,” because that is not fair to the [Netherlands Organization for Scientific] Research, the Chemistry Division.

Okay, but I have been for twelve years also consultant at the FOM Institute, so I had, still, the cooperation with the physicist there, so there was no problem.

So that went on, so the research was done both with the homemade FT-ICR, with the Varian MAT-711, then the MS9 was replaced by the ZAB instrument. [Fig. 7] And also, there, we did the <T: 05 min> experiment, for example, with negative ions. And we did an experiment where we had a singly-charged negative ion, collided it, and made a doubly-charged negative ion out of it. That was a very neat experiment because you don’t expect that.

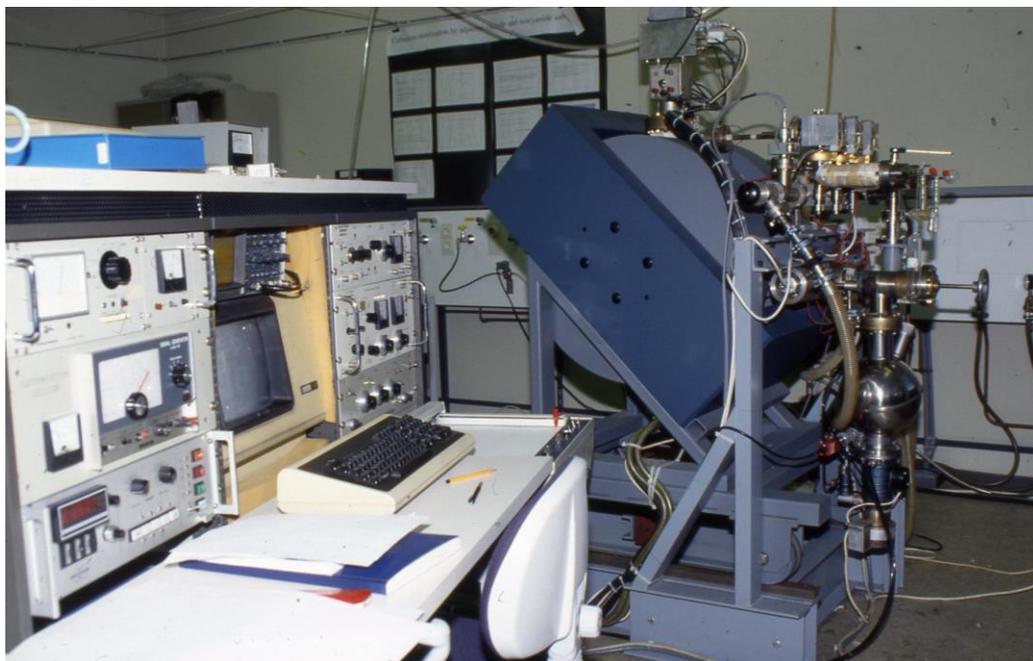


Figure 7. Home made FT-ICR from the University of Amsterdam

²³ Nibbering refers to *Stichting voor Fundamenteel Onderzoek der Materie*, the Foundation for Fundamental Research on Matter (FOM).

GRAYSON: Oh, how do you get the . . .

NIBBERING: No, but I remember the discussions in the group, and being next to the instrument, and then of course the conclusion was, “Why not? It might work.” And it worked. It worked.

GRAYSON: So somebody managed to stuff another negative charge in there?

NIBBERING: We could eject an electron from a negative ion to get to a doubly-charged anion. I thought that Helmut Schwarz was very excited, and there were other people. Okay, but so we did many projects with that instrument. We continued cooperation with the outside world, so to speak. Within the colleagues in the world. I have had a lot of cooperation also with Helmut Schwarz. It is simply too much to mention all these projects, but then I would like to have an additional thing on the ZAB instrument. I think it was a double-collision cell which I wanted to have because [. . .] with a double-collision cell you can eject, or let’s say deflect, the ion beam, and so you get the neutrals which, then, in the second cell, can be ionized. That is to study neutral molecules that came in. And I tried to get money for that not from the research organization from the Netherlands, but from the organic chemistry lab where I had a chair in organic mass spectrometry. And that gave some problems and I think that I made so much . . . I told about so much about it that the SON organization—SON is for the chemistry division of the national research organization, so typical for chemistry. They invited me, then, to talk about a possible transition from the University of Amsterdam to the University of Utrecht. And I had serious discussions with that.

Well the dean, at that time, I didn’t inform him because as long the discussions were going on it was not good to do you understand that.

GRAYSON: [Yes].

NIBBERING: But then we got a new dean, Jacob [A.] Moulijn, a young man from chemical engineering, in our faculty of chemistry. [. . .] And he found out that I had discussions with the people in Utrecht, together with the chemistry division of the [Netherlands Organization for Scientific Research], and he said to me, “How about we don’t let you go?”

And then I said, “Jacob, you can say that, but if the financial situation is not changing, then I’ll go.” And so he looked in the details about how the financial things were distributed over the chairs in organic chemistry. I had a very good relationship with the organic chemists of course. But then it turned out that it was not an equal partition of the money. That was my complaint also about it.

And then Jacob went to the Board of Trustees, and he managed to arrange a research institute for me. He said, “We don’t let you go, we offer you a research institute of mass spectrometry, and we will rectify the financial situation so you will get an operating grant of one hundred fifty thousand guilders per year. You will get two permanent staff members.” Of course I work all the time on myself with the group. “And you will get also some additional technical people.” So it was a very good offer, and I had, of course, to balance that with the opportunity to go to Utrecht. In the end—oh, [yes], first, of course, that was approved by the faculty of chemistry. They had them voting about it and they were unanimously in favor to keep me at the University of Amsterdam. And then I looked at the transition to Utrecht with all the difficulties also. So I decided to stay at the University of Amsterdam. <T: 10 min> And that made it all possible, in addition to the founding of the Institute of Mass Spectrometry, but also to get, now, money to upgrade ZAB 2HF with a quadrupole attached. And the detection system. That gave us the opportunity again to do new experiments, of course. I think the ZAB . . . well, first, field ionization kinetics, we did that with a much higher resolution than on the Varian MAT-711. But also we could use the instrument what Professor John Beynon described in his papers because he was heavily, also, connected with VG Micromass to develop the ZAB. We could do experiments like a complete level on its own.

For example, I would like to mention one experiment which is perhaps nice to hear. You made a methoxy anion in the ion source from ethanol. You did the mass selection so that you had a pure methoxy anion [beam]. Then you did a collision to convert it into a methoxy cation by stripping off two electrons. Then they passed the electric sector, which was then used as a means to purify the beam, of course. Realize there was an enormous reduction in signal, I think a factor of 10^5 . [laughter] Then that methoxy cation was decelerated to, let’s say, more or less thermal energies, and then ion-molecule reactions were performed in the quadrupole. We did it with several reagent molecules. And then we analyzed the products of these ion-molecule reactions, and we compared that behavior of the methoxy cation with that from its isomer, and that is protonated methanol, so that is CH_2OH^+ . We found that the methoxy cation reacted like a radical acceptor, electron acceptor, so electron transfer. Whereas the protonated methanol acted as a proton donor. It’s a completely different chemical behavior. So that was something like, you used the mass spectrometer as a complete laboratory on its own, synthesize, purify, do the reaction, identify the products, et cetera.

So then we are in 1988, that we became the research—the Institute of Mass Spectrometry—and before the MAT was upgraded, I think that was ’89 or something like that. But then, meanwhile, of course, also the Varian MAT-711 instrument became very old. And that induced me now to fight for a four-sector instrument. Because the four-sector instrument gave of course opportunities that you have a high mass, a front-end mass resolution. So it’s good to have a very purified beam, and then do collisional activation, et cetera, in the second double-focusing section. This was not for research. I mean the ZAB was most of the time used for research.

GRAYSON: Okay.

NIBBERING: I can say it was always a mixture between analysis for the organic chemists and inorganic chemists. But the ZAB was really used more and more for research, and the Varian MAT-711 had to be replaced. So I put it forward to get a new instrument, also to do advanced analysis for the organic and inorganic chemists. By the way, Jacob Moulijn said to me, “You have the operating grant of one hundred fifty thousand per year every year, and we let the organic and inorganic chemists pay for the analysis you are doing.” And, Mike, that gave a little bit problems in the sense that the colleagues didn’t like that idea. We didn’t overcharge, of course. That was not the case. But I thought that’s reasonable. If I found a doctor for a prescription, then I get a bill at home to pay, so why not for the analysis? Later on it was normal. [laughter]

GRAYSON: Oh [yes].

NIBBERING: [Yes], <T: 15 min> but I managed, then, to get the four-sector JEOL machine with all kinds of ionization methods on it—so electron ionization, chemical ionization, field ionization, field desorption, electrospray, not MALDI, of course, the activation unit for making the emitters. I must say the JEOL machine, that was a JMS 102A, I think, it is a marvelous instrument designed like the MAT. Very stable. If you have—a nominal mass calibration, that held for more than a year, and actually you didn’t have to recalibrate. But then sometimes you did recalibrate. For high resolution there’s another story. But I had the same results I heard from Shell in Amsterdam, there north of Amsterdam, the Royal Dutch Shell Research Institute there—that is the Royal Dutch Shell Lab. They had the same experience. And that happened in a resolving power of 50,000 in the first section and then about 80,000 the last section, as far as I remember correctly. So that was really a good instrument.

Then, meanwhile, also in ’86, we acquired a Fourier transform ion cyclotron resonance instrument from the Bruker company. The so-called CMS 47, 4.7 tesla. SoFT-ICR in addition to the homemade FT-ICR, we had, then, a commercial FT-ICR, so you could also then make ions outside the cell. because the FT-ICR homemade had only a cell and then you introduce your compounds by leak valves into the cell itself and then there the ionization reactions. But with the Bruker instrument you could externally make the ions and then guide them into the cell and do the reaction. You had post-valve addition of gas, to accelerate the ions and then do collisional activation, something like that. We developed a sustained resonance excitation which was also developed here at the Purdue University I think.

But that instrument was used purely for research. And what can I say more about it? You can imagine that having the interest in high front-end resolution, so that you can select a mass with a particular elemental composition under high resolution and then do a collision experiment and get the fragments and then analyze them by high resolution again. So that resembles of course a four-sector double-focusing instrument.

So we did that experiment. We did it by selecting the ions, applying so-called ejection pulses very carefully. So first you ejected a broad range of ions but avoided to eject the ions of interest. And then with fine-tuning, long duration pulses, you could get that high resolution to select. For example if you had a mixture of diisopropyl sulfide and an alkane, you could select, you could isolate ions with let's say from sulfur-containing ions and then isobaric ions containing only carbon hydrogen, and then do the collisional activation experiments.

We had a front end resolution of, in the beginning, of around—as far as I remember—20,000. And then after the collision, 400,000, which is normal for FT-ICR. Alan Marshall did this with his SWIFT [stored-waveform inverse Fourier transform] methods. But we did it by simply using well-defined pulses, and you know, to get high resolution takes time.

But that instrument gave us, also, the opportunity to do all kind of ion-molecule reactions again. One of them was, for example, to make noble gas dimers—radical cations of noble gases. **<T: 20 min>** For example, xenon (II) radical cation, or argon. And you could then replace one of the noble gas atoms in that dimer by a neutral organic molecule, or by two neutral organic molecules. For example, we made the dimer radical cation of water. The dimer radical cation of methyl chloride. And that was where for example on the two center of the [three] electron bond systems. Which is of chemical interest.

I mean, during my study I heard Professor de Boer talking about it, so many years before I did these experiments. The thing is, if you have a radical cation of sulfide, and you take a neutral sulfide, then you have an electrostatic interaction, because you have a positively charged species with a neutral species. But then you have then three electrons which you have to accommodate in orbitals. Now you needed two molecular orbitals and one of them is lower in energy, and the other one is higher in energy, because . . . but if you have two electrons in the lower level and one in the upper level then you would get bonding. These are stable species. But we found out, also, if you take a sulfide with a longer alkyl chain, for example, propyl or butyl, then the difference in energy between the lower MO and the higher MO decreased, so that meant also that the bond became weaker.

I must say that before we did it with a Bruker instrument we had done experiments on the homemade, because Helmut Schwarz approached us, could we show the existence of radical cation dimers? And let me see. And that was done with [K.D.] Asmus. We showed the two-center of the [three] electron bonds also in cooperation with Helmut. That was nice. What we also did in cooperation with Helmut was, you had the distonic ion, and distonic ion means that you have charges and a radical which are separated on different elements, and you can compare that with the normal isomers. So I remember if you take a methyl chloride or you take its distonic ion, that is CH_2 radical ClH^+ , $\dot{\text{C}}\text{H}_2\text{Cl}^+$.

GRAYSON: Okay.

NIBBERING: You could distinguish these ions by ion-molecule reaction with NO. With the normal ion you had only charge transfer. With the distonic ion you had the proton transfer. So

these kind of things, so we played real pure organic chemistry in the gas phase. There are many more examples which I described in the *Mass Spectrometry Review* article.

Well the instrumentation concerns during my career . . . so we had different sector machines and we had at least two ICR machines. The CMS 47 instrument has been upgraded at the end of my career. Not to a seven tesla, but let's say with better software. But we did run also—because I leave now a little bit about the chemistry we did. We can always see what we have to mention more but that we did also many analyses for not only our own laboratory but also for the faculty, also outside the faculty for colleagues in the Netherlands who didn't have the equipment but we also did run samples for <T: 25 min> David [N.] Reinhoudt. I would like to mention him, Professor David Reinhoudt from the University of Twente. [. . .] He was professor of organic chemistry there and was working in the field of supramolecular chemistry. And so we did run samples for David. But David also did see that MALDI was a method we didn't have, and it could be very beneficial for analyses of his compounds.

But I had asked the Netherlands Organization for Research, the chemistry division, to have a so-called new cell for the Bruker instrument, the infinity cell. That had a better performance. You can make a lot of things yourself but that So David found me and he said, "What do you think about . . . ?"

I said, "David, I've thought about it, but I cannot ask for money for that instrument because if you ask too many, too much different things, then it will fail in the end."

Then he said, "Okay, what I will do? I will apply for that instrument, try to get money also from the University of Twente. And if that is successful then I will put the instrument in your institute."

GRAYSON: Twente is . . .

NIBBERING: [. . .] They call it, in the Netherlands, UT, University of Twente. [. . .] So we managed that and with the permission of the Board of Trustees of the University of Twente, that instrument was indeed installed in our institute and it was a [PerkinElmer] PerSeptive [Biosystems] MALDI-TOF [time-of-flight] instrument, Voyager.

GRAYSON: Ah, okay.

NIBBERING: They're PerSeptive Biosystems [Inc.], and then a Voyager MALDI-TOF.

GRAYSON: Okay, PerSeptive Biosystems?

NIBBERING: [Yes].

GRAYSON: MALDI-TOF?

NIBBERING: MALDI-TOF. So we had used that simply for his work.

GRAYSON: Oh.

NIBBERING: Not only for his work but I mean his work was done on that, when he needed analysis.

GRAYSON: Sure.

NIBBERING: Was very nice.

GRAYSON: That's a good arrangement.

NIBBERING: It's a good arrangement and an exceptional arrangement because the Board of Trustees of the University of Twente allowed us to do that. Then, about the FT-ICR machine, I have to come back for that from Bruker. And because I was presenting a lecture in Uppsala, [Sweden], in 1988, I was invited by [Bo G.] Sundquist to give a lecture on FT-ICR. And then in the audience there was somebody who said, after the lecture, that was very nice, "I am your host tomorrow and you will be—" I knew that I would go to Stockholm [Sweden]. And he said, "I am your host and you will present a lecture now tomorrow for physicists only." And he said it was a very nice lecture, "but you have to leave out the chemistry."

GRAYSON: [laughter]

NIBBERING: And that was Professor Ingmar Bergström and he was the director of the Manne Siegbahn Institute. [. . .] He knew Jaap Kistemaker very well because he was a little bit younger, a few years but not more. And, so he picked me up at Stockholm station, then we went to the Manne Siegbahn Institute. Well Manne Siegbahn is a very well-known name in physics. [. . .] Manne Siegbahn? <T: 30 min> [. . .] He was a Nobel Prize winner I think the beginning of the last century. For x-ray, I think, also. But okay, and then he explained the reason why I was

there. He showed me the set-up and they would like to make a storage ring there with 50 meters diameter and then with Penning traps and FT-ICR traps in the ring to do [. . .] experiments on the highly-charged isotopes. Noble gas species or something like that. I don't know all the details because they had a cooperation also with the CERN [European Organization for Nuclear Research] in Geneva, [Switzerland].

GRAYSON: Oh, okay.

NIBBERING: And Ingmar and also [Heinz-]Jürgen Kluge from the University of Mainz in Germany but also working at GSI, the [Gesellschaft für Schwerionenforschung] and doing experiments in Geneva on short-lived isotopes, they had found out that I did FT-ICR and they want to do experiments in storage rings with these traps. That was the reason. Jürgen Kluge, I can spell also his name. [. . .] I have also written it down in the *Mass Spectrometry Review* paper. So you can always find it there. Ingmar was showing me then the lab and, well, he showed how they made Ar^{18+} .

GRAYSON: Eighteen?

NIBBERING: [Yes], argon, and remove all the electrons.

GRAYSON: Ah. [laughter]

NIBBERING: The higher charge the more energy it requires.

GRAYSON: Oh [yes].

NIBBERING: They liquefy themselves, the helium there, [preparing their own liquid helium]. And, well, Ingmar was talking to me, like, I said, “Ingmar I am a simple physical organic chemist, I'm not a physicist.” Of course, having that good relationship and being consultant at the FOM Institute in Amsterdam of course I learned how physicists were thinking. I mean you always end up in a potential energy diagram. But then he said to me, “What do you think about highly-charged ions?”

I said, “Well you have an Ar^{18+} , and you bring it in the neighborhood of organic molecules, it might explode.”

He said, “Okay, okay.” So we will apply for the project and then he will be the principal investigator. Because he was retired, and the chance to get funding . . . because that will be in a proposal submitted to the European Project, which you have to submit to Brussels, [Belgium]. So I did my part, and Ingmar made a nice proposal out of it. And he said, “You want already,” he said, “It might be the funding is less than 15 percent whether it will be successful.” But we were successful. We got the money and then we had group meetings either in Stockholm, or in Mainz, or in Amsterdam. And I had in the project for highly-charged ions making it an FT-ICR, I managed to get the physicist in my group from the Karl Marx University in Leipzig, [Germany], and his name is—the PhD student was—Holger[. . .] von Koding [. . .]. So Holger had to become acquainted to our idea of working as chemists.

GRAYSON: He’s a physicist? <T: 35 min>

NIBBERING: He is a physicist. We could, in principle, make Xe^{10+} with the Bruker instrument. But to make these highly-charged ions we needed, of course, high-energy electrons. So first, we tried with—Frans Pinkse, of course, was also involved, the lab technician—to fire electrons from outside into the cell. But that didn’t work because the magnetic field . . . they spread on the electrons. So Ingmar, when he heard it, he said, “You have to put an accelerator in the corridor and then fire the ions.”

But I said, “But Ingmar, how expensive is that?” That was two hundred thousand guilders or something like that, and that is impossible, for in chemistry we had one hundred fifty thousand operating budget and don’t ask as a chemist for this instrumentation at the chemistry division of the . . . you can imagine that they will say it’s physics. But Holger, well he tried to make these high-energy electrons in the cell. Well the electronics then was blown up, but that was repaired and there was no problem. But in the end he was able to make Xe^{5+} . But the abundance was too low to do experiments with. But what he found with a Xe^{4+} was that if that reacted with neutral xenon, then you did see not only a one electron transfer, because you isolate a certain isotope and then you look at the reaction product, and from that he could derive there was a single-electron transfer but also a double-electron transfer. And the double-electron transfer, I found it very interesting because a chemist always thinks in that case is that in stepwise reaction or a simultaneous, how you do it in one-step reaction. But I reasoned with Holger, and stepwise cannot be, because as soon as you make a singly-charged xenon with Xe^{3+} it will repel. So the cross-section to have, again, an electron transfer will be very low, isn’t it? So it must be a single transfer of two electrons.

But the interesting thing was, Mike, that if you go from Xe^{4+} to Xe^{3+} then you have only one single electron transfer. But if you go to Xe^{2+} then you see, again, a single-electron transfer and a double-electron transfer. Holger measured the rate coefficients for these reactions, and the double-electron transfer is more efficient than the single-electron transfer.

GRAYSON: That’s weird.

NIBBERING: That is—[yes]. We did it, also, with krypton and with argon. But the lower the mass, the more difficulty, because then it is not any more than the mass range of the FT-ICR instrument, [but also the frequency range].

GRAYSON: Sure, so you're doing this more . . .

NIBBERING: Because the cycle and frequency . . .

GRAYSON: You get smaller and smaller masses.

NIBBERING: Exactly, exactly, yes. I would have loved to continue these kind of experiments to really highly charged ions because I thought it is an even-odd, even-odd phenomenon.

GRAYSON: That's what I was thinking.

NIBBERING: And then having these experiments—and Holger was very careful. I mean, he remeasured many times so that we were sure what he was observing is . . . but I said to Holger, “We should have calculations on that.” So I approached Evert Jan Baerends from the Vrije Universiteit. I can spell his name but also, again, you will find the reference there. [. . .]

Well even also in cooperation with Evert Jan Baerends because one of my PhD students, [F.] Matthias Bickelhaupt, helped that his master degree study was with him. And so I phoned Evert Jan Baerends about is there a theory [which] could then explain why the double-electron transfer would be more efficient than the single-electron transfer? He said, “That is nice what you do, but you are working at <T: 40 min> thermal energies and there is not theory, not in the Netherlands.”

So then Jürgen Kluge—because you know Jürgen Kluge and Ingmar Bergström were informed about this work because of the cooperation. So Jürgen Kluge mentioned a colleague in Berlin and one in Kassel, [Germany]. Now I don't remember exactly the names anymore. But they got in touch with me. One of them listened and he said, “Nice, you are working in the wrong energy range; 500 electron volt is the minimum energy, then we can do it.” The other one would like to come over to Amsterdam but he said also you are in a very low energy regime—cannot be done. So that contact was lost because that . . . Later on I met a professor of theoretical chemistry who had retired. It was Laurens Jansen from the University of Amsterdam, but he worked in Switzerland, and it was a reception and so I talked with Laurens Jansen. [. . .] He was dean of the faculty of chemistry and was a member of the Board at that time that, was in

the end of the seventies. I knew him very well. I said, “Laurens, we have these observations and we do like to have theoretical calculation.” He said, “Professor [Lorenz S.] Cederbaum from [University of] Heidelberg.”

So I got in touch with Cederbaum in Heidelberg and explained by telephone what we observed. And he said, “Don’t worry, your observations are good.” Of course that was my concern. He said, “No, no, it’s okay.” He said, “But we cannot do quantitative calculations.” That’s how—only qualitative. But then in some way, I said to Holger, trying to get in touch with his students there but in some way that contact was also lost.

GRAYSON: So they found him in . . . the gentleman in Heidelberg, his name was . . .

NIBBERING: Cederbaum.

GRAYSON: Oh, okay.

NIBBERING: But then, of course—that is the reason why I mentioned Holger von Köding as a physicist—we had also a laser group in the faculty of chemistry. The physical chemists. I was interested to play with lasers, also, with ion beams. And that could be done on the ZAB instrument.

Then Holger was, of course, the right person to work on that because with the ZAB instrument you could decelerate the ions, say, before the ion quadrupole, and then fire a laser to the beam, and then look at the fragments by using the quadrupole. That was the idea. So Holger started to work on that, and I must say that very helpful was also Piet [G.] Kistemaker [. . .]. It’s the same name as the Jaap Kistemaker [. . .]. He was appointed, when the Institute of Mass Spectrometry, was—started to work. I said to Jacob Moulijn, who I mentioned before, “We should have cooperation with the FOM Institute,” and therefore Piet Kistemaker was appointed as a part-time professor in physical mass spectrometry.

My chair was, by the way, changed from organic mass spectrometry into chemical mass spectrometry. But Piet was, of course, also, the right colleague to work on that laser experiment to change the instrument for laser interactions with selected ion beams. Now the thing was, of course, to decelerate the ions more properly for the quadrupole. So a new lens system was made, because you know if you decelerate ions they start to...

GRAYSON: [Yes], they’re not going to sit there idly being nice.

NIBBERING: So it should be a well-defined ion beam. They managed to do that. And

therefore we have done experiments—cross-beam, laser ion beam—and then <T: 45 min> collect or look at the fragments through a quadrupole. That was the construction of that instrument. Measurements were done by Ilse Aben. [. . .] She was a postdoc in my group coming from the Vrije Universiteit in Amsterdam, and had studied physics there. So that was very helpful of course.

GRAYSON: Is the interaction between laser beam and your ions is . . . that's not going to be very productive, is it?

NIBBERING: No, exactly. No, no, because one of the problems we found out was, you had spontaneous metastable ion decompositions, in addition to the laser-induced dissociations. So Mike, what is it that we make always the following comparison? You would like to know the weight of a captain of a ship. You weigh the ship plus captain, then you weigh the ship itself, and from the difference you find the weight of the captain. [laughter] So this was the case with these kind of experiments.

GRAYSON: The hard way. [laughter]

NIBBERING: The hard way and so therefore . . . these experiments were done by Ilse Aben. And therefore Holger was asked to make an orthogonal [acceleration] time-of-flight coupled to this. So you do the laser experiment and then deflect the ions in the orthogonal time-of-flight to get rid of the metastable ion contribution.

GRAYSON: Yes.

NIBBERING: So Ilse had done it with the quadrupole, and Holger changed the quadrupole in an orthogonal time-of-flight. And we have done experiments with that instrument, and they were successful. At least they proved that it worked. And I had the end of my career. [laughter]

GRAYSON: You actually took the existing four sector instrument—with the quadrupole on the end and you replaced it with time-of-flight?

NIBBERING: [Yes], orthogonal time-of-flight.

GRAYSON: So you got a sector instrument, front end? Was there a . . .

NIBBERING: Orthogonal.

GRAYSON: . . . time-of-flight.

NIBBERING: And the timing, of course, to put the laser on the selected ion beam and deflect the ion . . . deflected ions into the time-of-flight [. . .] you can only do that by computer, of course. The timing of it but . . . and again you can always look back in the *Mass Spectrometry Review* article, that it is described in a brief way, but it worked but then I had the end of my career.

GRAYSON: I still want to talk about this laser interaction thing. So I mean, you had to pick a frequency that was going to be effective.

NIBBERING: This was an ultraviolet laser.

GRAYSON: Okay. You made that selection based on the idea that you knew that this would be interacting with the molecules or the ions in a way that would cause the decomposition to occur?

NIBBERING: Sure, sure, ultraviolet laser, yes. There was money for the—to buy these lasers. Because a colleague in physical chemistry, he managed to get money to work with lasers in the faculty. So several colleagues could make use of it among others and myself.

GRAYSON: That makes it very powerful? I mean, that would be reasonably powerful, I guess, since they were . . .

NIBBERING: [Yes].

GRAYSON: Okay. Very good, well that's . . .

NIBBERING: I think I have now described more or less all the instrumentation.

GRAYSON: Right.

NIBBERING: The changes that were made, the aim of the . . .

GRAYSON: And I think so, yes, yes, yes. Are there any other items that you want to discuss—outside of the instrumentation part of your . . . You've talked a lot about interactions with different people, and the importance of meeting different people, and going to travel, and working in different laboratories. I noticed that you had done some work with pyrolysis.

NIBBERING: Okay, yes.

GRAYSON: What was that all about?

NIBBERING: That I can immediately explain it to you. Pyrolysis mass spectrometry had been developed—Curie-Point pyrolysis—at the FOM Institute in Amsterdam by [Henk L. C.] Meuzelaar and Jaap Kistemaker. And how did I get in touch with that? Joseph Huber—whom I mentioned in purchasing the Varian MAT-711 instrument, the analytical chemist—he had a student, and he would like to make use of the <T: 50 min> pyrolysis mass spectrometry which they made at the FOM Institute. And Joseph said, “Well, look at it.” And of course I thought . . . later on because Joseph didn't continue that cooperation or contact so he transferred it to me.

Then I was talking with Henk Meuzelaar who moved to the United States to Utah, Salt Lake City, but he was a medical person.

GRAYSON: Right.

NIBBERING: Now you know Henk Meuzelaar?

GRAYSON: [Yes].

NIBBERING: And so I had Henk Meuzelaar at home. And then we were discussing it, and I said to Henk, “What I would like to do in pyrolysis is let us take a look at a molecule of methionine.” Why the interest in pyrolysis? Because in the electron-ionization work worldwide, there were people saying, well, that mass spectrometry resembles pyrolysis. But I never accepted that idea because in electron-ionization you make ions and their reactions are driven by a radical charge. And in neutral molecules there is no charge. So is it the same as electron-ionization pyrolysis? And that was a good opportunity, of course. So I said methionine. Why?

Because methionine was studied by us by high resolution mass spectrometry on the Varian MAT-711 instrument. And we had measured, manually, on the high resolution conditions the elemental composition of the ions from the molecular ions down to the mass forty range.

GRAYSON: Okay.

NIBBERING: The reason was that Bob [Robert A. W.] Johnstone in England, from Manchester, he had written a paper on methionine and it was very critical and skeptical with respect to a paper published by [Harry J.] Svec and [Gregor A.] Junk—Junk, I think.²⁴ Svec, Harry Svec from the Ames, Iowa.

GRAYSON: Oh [yes], sure.

NIBBERING: I didn't mention him during the trip that I made through the United States because I visited Thomas [H.] Kinstle. That was my host, but I had met then Harry Svec. I think, Mike, he was working on an instrument where you made positive ions there, and negative ions there, in opposite directions. But later on I did see that paper, and they used the concept of charge localization to account for the fragmentation of molecular radical cations. Also Beynon and [Dudley H.] Williams, they have published a paper on that and that a radical plays an essential role. And we used that concept for interpretation of mass spectra. You know very well, it is a concept? Is it a theory? It's a concept, it works, is it then true?

I mean if you were to talk with theoretical chemists they will say the charge is not localized, it is distributed. But it was a workable concept. And so Johnstone had measured this mass spectrum with I think with an AEI MS9 instrument coupled to a data system. But if you put a threshold too high then you will miss small peaks and therefore he found sometimes ions with only one elemental composition. Whereas we by manual peak matching, found four compositions.

GRAYSON: Oh boy.

NIBBERING: For some of the peaks. We said the charged radical localization, it works. Because he was skeptical and didn't—he said, “No, no, no.” But we said that Harry Svec, his

²⁴ T. W. Bentley, R. A. W. Johnstone and F. A. Mellon, “Mass spectra of organic compounds. IX. Evidence against charge localization in the fragmentation of methionine and selenomethionine,” *Journal of the Chemical Society B* (1971): 1800-1803.

paper was, well, very explicable by using the concept of charge localization. But now the mass spectrum of pyrolysis of methionine resembles very much an electron ionization spectrum.

So that gives you an idea. Pyrolysis still resembles, then, EI. But that is a completely different behavior because there we did the elemental composition, of course, by labeling of the product ions. And for example, if you look at the ion, molecular ion of methionine, it will show a peak at mass 116 by loss of H_2NOH . <T: 55 min> [. . .] In the pyrolysis you find an ion then by expulsion of a nitrogen-containing fragment. In the electron ionization spectrum that is the loss of a methionine carbon monoxide, so quite different. Then I have to look it up exactly. There were more peaks . . . I remember 101 and 104. So seemingly they were the same masses, but the elemental composition was different. So we simply could say no, it is different.

GRAYSON: And this occurred in the pyrolysis?

NIBBERING: Curie-Point pyrolysis, I have it here, hydroxylamine, that is the one, two elimination. Hydroxylamine is NH_2OH . That was upon pyrolysis and upon EI it was a methyl radical and then a molecule of water. Molecule of water and methyl radical. Sorry, not CO but a molecule of water and a methyl radical. There were other . . . 101 for example, that was . . . we had the elimination upon pyrolysis that was due to the loss of a molecule of water, carbon monoxide and molecular hydrogen, whereas methanethiol was eliminated from the molecular ion of methionine, so completely different. So that was a very nice experiment.

And then Jan [W.] Dallinga . . . this work was done with Maarten [A.] Posthumus. He was a PhD student of Huber, but I became the supervisor of Maarten Posthumus. [. . .] And, you know, we continued that Curie-Point pyrolysis at the FOM Institute with Jan Dallinga, a PhD student from my group, so we looked at carboxylic acids and aromatic compounds and found also differences between electron ionization and pyrolysis. But then we stopped. I mean, you had to put in proposals for the Science Research Organization in the Netherlands and this was a cooperation really to do that with the physical chemists, and physics. But the world of physics and chemistry is different and it holds also for these organizations.

GRAYSON: Oh [yes]. I can imagine, particularly when it comes to grant awards.

NIBBERING: Exactly, exactly, so that was one and that was okay and it gave me enough confidence to say pyrolysis is different from electron ionization.

GRAYSON: Well I mean I think your initial reaction is that it should be. There may be one or two things that are going to be commonly produced but they're probably produced in a completely different way.

NIBBERING: Yes, yes, yes, yes.

GRAYSON: One thing I wanted to ask you about earlier that I didn't get a chance and that is if you're doing these organometallic compounds a lot of times they kind of tend to gum up your ion source because the metal, to make the ion, you can start plating out the metal on your insulators, and then you start to get . . . is this a problem at the . . .

NIBBERING: No, I must say that we cleaned very, very frequently the ion sources. We had simply a scheme and also we always looked at backgrounds. Metals, we did some organometallic ions also in the FT-ICR but there it's less critical. At least for the sector instruments we have these high potentials and that the insulators failed to work as they should be. Now, Mike, the Frans Pinkse, the lab technician, he was very careful all the time, so better to spend time on cleaning the ion sources than to always in a hurry to do measurements.

It was standard of course also on Friday afternoon, the machines were set on baking. It was not only organometallic were but also . . .

GRAYSON: Sure. <T: 60 min>

NIBBERING: . . . sometimes you had molecules, then you looked at the background on Monday morning and it was a clean instrument; heating, heating of course, heating.

GRAYSON: Oh [yes].

NIBBERING: Tape it, they . . . also with the ICR, tape it and heat, get rid of all the . . . because that is what physicists don't like is they talk with organic chemists. That was also what Ingmar Bergström was saying, "That stuff, dirty, dirty."

GRAYSON: [laughter] So you had a very specific lab regimen that you followed to keep the instruments . . .

NIBBERING: Frans Pinkse and I were on the same line. Let's say it should be clean. And it requires time, but then you lose less time than when you don't do it because then you end up in a mess.

GRAYSON: And the data—you can't trust the data you get.

NIBBERING: No, exactly, but also, for example, Andries [P.] Bruins, one of my PhD students, we worked on the so-called benzyloxy butane species. That is, you have a benzyloxy at one side, benzyloxy the other side, separated by a chain of four methylene groups. We did study that for basic reasons, basic ion chemistry. What we always did, I liked that, have symmetrical molecules, because this was a symmetrical molecule, but then put ^{18}O on one side and ^{16}O on the other side. Put deuterium at one side and hydrogen there. And then see the interactions. And that was very nice, because then that gives an eye opener how complicated the chemistry then is.

GRAYSON: I can imagine.

NIBBERING: You can imagine. There are many examples from my group where we did it, but the compounds on these, they were not volatile so you can imagine we did these experiments in the AEI machine and that was not like we take the molecular ion. Now we did a number of experiments—which was time-consuming, of course—looking at metastables, now you could do a collisional activation reaction, you looked at it, then baking, of course, we knew that these compounds were not very volatile and polluting the source. So measurements were done on Friday for these molecules. Monday, then we assumed it was by heating the whole weekend that we had gone and you looked and it was no background anymore except a water or something like that. And then three weeks later somebody came in with an analysis, an organic chemist and Meuzelaar, I mentioned him yesterday who was running the analytical work for the lab at that time. And suddenly the compound of Andries' appeared in the spectrum.

So he said, "What's going on?" But then we had a compound which simply replaced, removed it from the surface because it was better bonded to the surface and then pushed and then . . .

GRAYSON: It was deposited and exchanged? Surface exchange.

NIBBERING: . . . surface exchange. Because the binding of the other molecule was better than from Andries'. He said if you would know everything you could use that for making clean surfaces.

GRAYSON: Oh [yes]. [laughter]

NIBBERING: [laughter] Crazy.

GRAYSON: Those are the interesting things. What's with the three-electron bond work? There is a paper were you working on this three-electron bond?

NIBBERING: Samuel [P.] de Visser did that. That was on sulfur containing ions.

GRAYSON: Ah, okay, the sulfur work?

NIBBERING: Sulfur work. And the chloride was interesting because the methyl . . . we had interaction with Helmut Schwarz about the two center, three electron bond that was an experiment done before Sam de Visser did the disulfides.

GRAYSON: Oh, okay.

NIBBERING: But as I said before from Professor de Boer already in the past, far past, I learned that the three electron bond—two centered electron bond—was very interesting because they had these so-called colloquia where students had to scan the literature and give a presentation. From that I remembered that, and it was interesting. But methyl chloride was an interesting one <T: 65 min> because we found two species. Well the methyl chloride dimer was made, as I said, taking a noble gas dimer, replace then the noble gas atoms in the dimer by methyl chloride. So you get the radical cation dimer of methyl chloride. Then we looked at its properties, looked at its bond dissociation energies, and we found there are two species. That is, in dimethyl chloride where the chlorine atoms are bonded to each other in a two-centered, three electron bond, so there is a symmetrical structure, and the other one was a distonic ion. That means a CH_2Cl proton bonded to normal methyl chloride: $\text{CH}_2\text{ClHClCH}_3$. We studied, by ion-molecule reactions, the behavior of these ions. We determined, of course, the strength of the bond, of the three-electron two-center bond. We found that the two-center, three-electron bond species—so, the symmetrical one—was responsible for electron transfer. If you take a methyl chloride with a neutral methyl chloride, you can have an electron exchange. That species was imported for the electron exchange whereas the other one, the $\text{CH}_2\text{ClHClCH}_3$, that was the response of a proton transfer, [yes]?

GRAYSON: Okay.

NIBBERING: And, there were also calculations done at [the] Gaussian [level of theory] . . .

and that fitted well with our experiments. So we could say the bond dissociation, see for the symmetrical structure is higher than for the proton bond structure. But the funny thing is [. . .] the two-centered three-electron bond species, how is that transformed into CH_2 radical ClHClCH_3 ? That is a neutral methyl chloride, is dragging a hydrogen atom from the carbon atom to the chlorine, without changing their atoms. It's really helping to get the hydrogen atom moving from carbon to chlorine. And the same was shown in the distonic ion because this is a distonic ion you are making from methanol. Methanol as a distonic ion is CH_2 radical O, let me see, H_2^+ , whereas methanol is normally CH_3OH . And in that case that was proven by the group of Henri [E.] Audier—who I now know very well from Palaiseau, [France], near Paris, the École Polytechnique. Where a water molecule, if you do it in a chemical ionization source and water molecule, if that sees an ionized methanol species, then the water molecule says, okay, I pick the hydrogen atom from the carbon atom and move it to the oxygen. Without exchanging its hydrogen atoms with that hydrogen atom which is moving from carbon to oxygen. So it is a catalyst.

GRAYSON: [laughter] That's pretty strange.

NIBBERING: That is strange but theoretical chemistry helps to understand because there has been . . .

GRAYSON: They've done calculations?

NIBBERING: [Yes].

GRAYSON: Okay.

NIBBERING: Nowadays, nowadays. If you do this kind of work without doing calculations, impossible . . . no, no, no. *Always* calculations and they are very accurate up to two kilojoule per mole. So both, let's say . . . you always would like to know in a bimolecular ion-molecule reaction what is the energy of the starting material—the ion plus the neutral. Then you would like to know the transition state, and then you would like, of course, to know the energy of the products. And from that you can learn that **<T: 70 min>** sometimes the activation energies if you call it or to pass the transition state is too high, so you have to go to other transition states.

So it is very helpful. But also for unimolecular reactions, unimolecular decompositions. If you excite an ion, then to know the activation energy is the threshold, where you have to pass the barrier to come to the products. Then you can exclude many reaction pathways because they are energetically unfavorable .. That part has been developed over all the years if I look back since my master's degree study what I wanted to have to do these reactions I had mentioned in

the beginning. That has been fulfilled. Not by me, but I mean by the developments also in theoretical chemistry, it's very helpful. There is a symbiosis there between these two fields. And they can also calculate larger systems. Although if you would like to have precise calculations for large systems it becomes difficult. It is still difficult.

GRAYSON: Oh [yes]. Well there's a limit and there's more power coming with computers and software, but still . . .

NIBBERING: But you have, for example, the density functional theory is heavily applied. You have *ab initio*, [John A.] Pople and his group . . . [yes], Pittsburgh, I think, yes. But the density functional theory, that helps to reduce the amount of computer calculations . . . they are more simplified. But there is, well Matthias Bickelhaupt who received his PhD with me. He did his master's degree in theoretical chemistry with Professor Evert Jan Baerends, whom I mentioned. So Matthias has a lot of experience with DFT theory but also with *ab initio*. And so when he joined my group he did experiments with the homemade FT-ICR and then did also calculations, of course. And that also induced Sam de Visser to do calculations for the two-center three electron bonds of methyl chloride and the sulfur compounds. That was then also possible.

And since then that was done in my group so you see it is . . . well, let me say the following about a career. If you are appointed as a professor of let's say organic chemistry or mass spectrometry, then you are, well, limited because you have to work as long as you are on the chair on mass spectrometry. You cannot say suddenly, "I will do something else." So my method was every five years [. . .] to get something new in the group without throwing away the good shoes you had. And in that way it was built up. So I'm still excited about electron ionization. There's a method which is still used in GC-MS but I think the chemistry, when you apply electron ionization the chemistry is very transparent.

GRAYSON: I guess electron ionization will be with us for forever, huh?

NIBBERING: [Yes].

GRAYSON: It's a good method for . . . it works for what it's good for and it's important. Well we've covered a lot of material here. I was curious we didn't say much about your patent experience, if any. Have you had any patents or bothered with patents, or is patenting . . .

NIBBERING: [Yes]. We have thought about making patents when we build the FT-ICR tricks there. But a university is not suited to handle that—at that time. So no.

GRAYSON: Okay.

NIBBERING: So we have a very open. I mean, let's say the emission control unit, [for example].

GRAYSON: Oh, [yes].

NIBBERING: We thought that was an interesting thing, isn't it? So we showed it to the VG Micromass people because we bought the VG Micromass machine and we wanted to have field desorption on it.

GRAYSON: Right.

NIBBERING: But they were not so good at field desorption at [VG Micromass]. We showed them [our unit as well]. We showed <T: 75 min> also MAT, no problem. Because also, we were aware that if we needed the source file for the software we could get it. We didn't misuse that trust. I think I used the word, 'trust.' But then they said, "That's very nice of course but it's too expensive to commercialize that." That is where I didn't have to bother about, isn't it?

GRAYSON: [Yes]. They ought to think in those terms.

NIBBERING: [Yes].

GRAYSON: You have to sell it and it's money.

NIBBERING: [Yes].

GRAYSON: Well, I mean, the other problem is that if it worked and made that ionization method more useful maybe they could have made money on it.

NIBBERING: Now with respect to field desorption. [H.] Bernhard Linden from [Germany], he got his PhD with Beckey and he has developed LIFDI, liquid injection field desorption ionization.

GRAYSON: [Yes].

NIBBERING: Well, he has presented that in the last year. Also the, ASMS, and that has become a very user-friendly method to . . . well, operate field desorption. Also for let's say air sensitive compounds or very labile organometallics, these examples where other methods fail but that works. And, yes, I know that Bernhard also sells these devices to industries.

GRAYSON: That is an issue in the ionization area; sometimes you want a very soft ionization technique . . .

NIBBERING: [Yes].

GRAYSON: . . . and they're not always able to be as soft as you would like.

NIBBERING: Well I would say the softest ionization method which I have found from experience is field desorption.

GRAYSON: Okay.

NIBBERING: That's really soft? But we know the challenges. I think it has been made [more] user-friendly but then, of course, the masses which you can do with it compared to electrospray . . . and MALDI . . . their masses are in the lower end. But analytical chemistry, there is not any instrument which can do everything. There's not any method which can do everything. Forget it.

GRAYSON: [Yes].

NIBBERING: What I am impressed is by the work . . . well I'd been this week at the Purdue University and DESI with Graham Cooks. His group has developed . . . DART, developed by [Robert B.] Cody. [. . .] Direct Analysis in Real Time I think is the term for DART. And then DESI [desorption electrospray ionization] by Graham.

But now paper spray, the paper spray method where they analyze these molecules by dipping it on a paper and put in potential and get the ions into the mass spectrometer. It is very impressive and I must say that I was glad that I was, after so many years, again in the lab of Graham. I said to him, "I see the time coming that you will have these kind of very simple—these are not—they are still mass spectrometers but they are so miniaturized." That will be a standard thing to have in organic chemistry labs, in clinical labs, in medical centers or in hospitals. It will take, of course, an additional years to commercialize it in a way that you have an instrument like a black box which everyone can use, but I think that time is coming.

And I must also say they use a lot of chemistry to, let's say, get good results out of it. I mean again if you do chemical ionization you can do it with CH_5^+ but you can do it also with C_4H_9^+ and so you can do it with other reagents. For me it was a pleasure to see that they simply use organic chemistry to get very good results via use of these ionization methods. Chemical approach, combined with instrumentation. Simple instrument—no, not simple. In depth of course you have to take care of many things but, no, it is very elegant I think.

GRAYSON: Well Graham believes they should have a mass spectrometer in every garage or dungeon or something.

NIBBERING: No, but really it is impressive. [laughter]

GRAYSON: Well he's an impressive fellow, isn't he?

NIBBERING: [Yes].

GRAYSON: No doubt about that.

NIBBERING: [Yes]. <T: 80 min>

GRAYSON: Let's see, all right. So we've been talking pretty much about mostly the experimental areas. Do you have any publication you consider to be your most important—single most important publication?

NIBBERING: [Yes], I have thought about it of course, when I did see that question. The thing is that is, of course, a personal thing, of course. I have listed a number of them.

GRAYSON: Okay, can I have the list?

NIBBERING: But it is in Dutch.

GRAYSON: [laughter]

NIBBERING: No, but I can....

GRAYSON: Well or we can . . .

NIBBERING: Well I simply can mention the list?

GRAYSON: I've got your bibliography here. So I can tick them off of here from there.

NIBBERING: But it is in Dutch but I can read it to you.

GRAYSON: But if you've got the dates and what-not I can just pick them off out of this group here.

NIBBERING: Okay, now I think that the first publication on 1-nitropropane.²⁵ The master degree study.

GRAYSON: So that was one of the earliest?

NIBBERING: Yes. Why? Why, Mike, because we simply did give a scheme based on the deuterium labeling that the McLafferty rearrangement was occurring in a stepwise fashion. Then I think also the phenylethylether and phenoxyethyl chloride stuff but that has a lot of publications. It started with Carla Theissling.

²⁵ Nibbering, N. M. M., Th J. de Boer, and H. J. Hofman. "Mass spectrometry of nitro compounds: Part I: Mass spectra of α -, β -and γ -deuterated 1-nitropropane." *Recueil des Travaux Chimiques des Pays-Bas* 84, no. 4 (1965): 481-487.

GRAYSON: In nineteen . . .

NIBBERING: . . . seventy-four, I think [. . .]. And that was also work . . . who was involved? So Carla Theissling is a PhD student, Michael Gross and Dave Russell.

GRAYSON: Okay, Gross and Russell, I'll just make a note here, Gross and Russell.

NIBBERING: [Yes], Jan van der Greef.

GRAYSON: Jan . . . that's the same time period, '74.

NIBBERING: Something like that, yes.

GRAYSON: Okay.

NIBBERING: The key word is phenoxyethyl chloride.

GRAYSON: Let's see. Unfortunately this is the slowest dumb computer because I can . . . if it would work. [. . .]

NIBBERING: I mentioned already a few of them, so I can . . .

GRAYSON: So we're going to look for phenoxy?

NIBBERING: Phenoxyethyl chloride or phenoxyethyl halides.

GRAYSON: Okay, a phenoxy search first for any deal.

NIBBERING: Because you can select them from the list then then.

GRAYSON: So let's load this up and we've got . . . I've got '74. Well there's a collisional activation study of $C_6H_6\dot{O}^+$, ions generated from molecular ion [of 2-phenoxyethylchloride]. That was in '77, Borchers?²⁶

NIBBERING: [Yes], that was a cooperation with Bonn. Now you see the effect that I didn't get the instrument and that I decided to do cooperation outside the Netherlands and Carla Theissling was involved in that.

GRAYSON: Okay. So that's one of those?

NIBBERING: One of those.

GRAYSON: Phenoxy papers?

NIBBERING: Yes.

GRAYSON: Okay.

NIBBERING: And, Wim [J.] van der Hart in the end and Michael Gross with Dave Russell, it was a difficult problem.

GRAYSON: Here it is.

NIBBERING: You know, Mike, let me simply say the reason why we did study that compound. When I started to work with the drift cell ICR, I did the <T: 85 min> experiments myself because there was no group at that moment. Then I decided to study phenylethyl ether, and phenylethyl ether has two possibilities . . . there is a hydrogen atom transfer from the methyl group to the aromatic ring and then elimination of ethylene.

GRAYSON: Okay.

²⁶ Borchers, F.; Levsen, K.; Theissling, C. B.; Nibbering, N. M. M., "A collisional activation study of $[C_6H_6O]^+$ ions generated from the molecular ions of 2-phenoxyethyl halides," *Org. Mass Spectrom.* **1977**, *12*, 746-50.

NIBBERING: That is the McLafferty rearrangement giving you the the keto form of phenol, keto form. Or it is transferred to the oxygen atom and then it produces phenol.

GRAYSON: Okay.

NIBBERING: And it turned out by our molecule reaction studies that only phenol was formed.

GRAYSON: I see.

NIBBERING: No cyclohexadienone. And then we said, okay, let us now put in an halogen atom. One of the hydrogen atoms from the methyl group replaced by a halogen, because then you have an atom with a lot of electrons around it that doesn't like the oxygen atom. So we forced now the system to get the hydrogen atom transferred to the ring and not to oxygen. And that has taken many years [to solve]. I think that publication was in '82 with Wim van der Hart; in the end we could show, definitely, that there is phenol formation but there is also cyclohexadienone.²⁷ And the phenol formation is via an intramolecular catalysis. Well that is . . .

GRAYSON: Okay.

NIBBERING: And I think why I'm excited about it, regard this as an highlight, that is because in . . . I think that was Pierre Longevialle from France. He had, at the end of the seventies, around '80, 1980, he had firm evidence for the occurrence of ion-molecule complexes, during the unimolecular dissociation of ions.²⁸

So, you have a transition from unimolecular to bimolecular. If you talk about a unimolecular dissociation then in the end this ion-molecule chemistry which is going on, so the barrier between unimolecular and bimolecular chemistry . . . you call that "on very thin ice".

²⁷ P.N.T. van Velzen, W.J. van der Hart, J. van der Greef, N.M.M. Nibbering and M.L. Gross, "Photodissociation study of C₆H₆O⁺ ions in an ion cyclotron resonance spectrometer." *Journal of the American Chemical Society* 104 (1982): 1208-1212.

²⁸ Longevialle, Pierre, and René Botter. "Evidence for intramolecular interaction between ionic and neutral fragments in the mass spectrometer," *Journal of the Chemical Society, Chemical Communications* 17 (1980): 823-825.

GRAYSON: [laughter]

NIBBERING: Now that phenoxyethyl chloride . . . we had also an idea about an ion-radical complex with that work by Carla Theissling, but we excluded that because it didn't fit with the radical substituent effects which were applied. But if you look at the work [Tom] Morton around the same time here in the United States then they would say, phenoxyethyl chloride; oh [yes], that that reacts [in a radical ion] complex, when you do the molecular ion dissociation. But the fact that we find still the formation of cyclohexadienone, so the keto form of phenol, says it is not only ion-molecule chemistry. On the contrary in that case we have covalently bonded structures, so that means they're ion-molecule complexes. You have to be careful, very careful in the interpretation.

GRAYSON: Oh [yes].

NIBBERING: What is really going on.

GRAYSON: Oh, definitely. There's no question about that.

NIBBERING: So that was a highlight and then of course the drift cell ICR, I think that wasn't highlighted, that we modified the drift cell FT-ICR machine. But that has to do with the highlight in my career that is the trip through the United States in '69. That's a highlight. And of course also the highlight is the few months that I was a visiting scientist in Fred McLafferty's lab in '74. The fact that I had then the opportunity to go to the ASMS in Philadelphia and the fact that we met Michael. As simple as that. Then of course the highlight is the construction of the homemade instrument within one year and a day. You can imagine that.

GRAYSON: That's very impressive.

NIBBERING: Then of course also if I go to chemistry, the protonated methanol reacting with neutral methanol. That I can explain to you <T: 90 min> because Henis from St. Louis [Missouri], Monsanto, he had studied the reaction of methanol and protonated methanol and he proposed a reaction which we thought is for organic chemists not so attractive. We had more the idea that it would go through an Sn2 reaction. That's in organic chemistry well-known [reaction]. Whereas, that possibility was not taken into account by Henis. I don't know whether he's still alive. Now we did the following experiment to show that it was due to an Sn2 reaction that was Jan [C.] Kleingeld, so if you look under the name [Kleingeld], you find a number of papers written with him, but it was one of the first experiments we did with the homemade FT-

ICR. If you take normal methanol then, we have an 0.2 percent O-18 labeled molecules, naturally occurring O-18 and 99.8 O-16 and there is some O-17, but it is 0.04.

GRAYSON: [Yes].

NIBBERING: Now, if you now make ions from methanol with electron ionization we have a relatively long pulse of electrons making the ions that you fill the trap with a lot of ions—too much. It is overloaded. But then you start to eject all the ions from the cell, except the protonated methanol O-18 and then it is in a bath gas of $\text{CH}_3^{16}\text{OH}$ for 99.8 percent, isn't it?

GRAYSON: Ah, okay.

NIBBERING: So, now you can see what the reaction of protonated methanol O-18 is doing with neutral methanol and if there is an $\text{S}_\text{N}2$ reaction then the neutral methanol will attack the methyl group of the protonated methanol and will substitute the water molecule. So, the water molecule was getting off and so you get unlabeled protonated dimethyl ether. And that was what the experiment was saying. So, it was nice so we had evidence for that.

Of course in the complex because nature has to be cooperative with you there was a little bit exchange but not so that it destroyed the idea. And then that triggered, again, publications from American groups, of course some of them said, "No, no, it is not an $\text{S}_\text{N}2$ reaction, that is too high energy." Because in a substitution reaction you have to change the [hydrogen atom positions] among the carbon atom and that requires a high activation energy, way too high; but in the end the theoretical chemist said you are right. [laughter] It is an $\text{S}_\text{N}2$ reaction.

GRAYSON: Good.

NIBBERING: Interesting was I think a highlight; the formation of a hydride solvated water molecule, H_3O^- .

GRAYSON: Hydride solvated . . .

NIBBERING: H_3O^- .

GRAYSON: Oh, [yes], okay.

NIBBERING: You know, Mike, many things are found by accident. Well I—perhaps it's not the right word, but you understand what I mean?

GRAYSON: Serendipity.

NIBBERING: Serendipity, yes. We were interested to do the so-called Meerwein[-Ponndorf-Verley] reduction. Again, you can look in the paper. But it is that you could take a methoxy anion and you react it with CH_2OH and you label one of the systems and one of either the ion or the neutral. And look whether you have a hydride transfer, H^- transfer from the ion to the neutral. There is a Meerwein-Ponndorf-Verley reduction known in organic chemistry. So, we use also organic chemistry as a guide to look. [. . .]

But to make the methoxy anions you needed water, so you started with making OH^- . And Kleingeld did the experiment and suddenly found that <T: 95 min> there was a peak at mass 19.

GRAYSON: 19?

NIBBERING: Negative ion; but we knew that the frequency of the FT-ICR machine could interfere with the frequency of the radio station in Scheveningen [Netherlands], because you could pick up signals of course from outside and it was a real signal.

So, immediately we said, is it really an ion or is it perhaps a picked up signal? Let us label with deuterium or O-18. Then we found the following . . . let me take a look at the reaction that is easier for me because then I can use the words. [. . .] So what is the reaction? The OH^- will react with formaldehyde. [. . .] Again, the formation of H_3O^- . And if you label with deuterium and unlabeled formaldehyde then you will find that the reaction product does contain the deuterium atom. And if you a label O-18 in the formaldehyde then you will find . . . let me see that is a proton abstraction of [from formaldehyde] that gives you C^{18}O plus H_3O^- . HC^{18}O^- is actually carbon monoxide carrying a hydride. Then it sees the water molecule and says—because that complex cannot separate because that is endothermic. But then HC^{18}O^- sees that neutral water molecule which is formed in the first step and says, “Take over the hydride, the water likes the hydride.” So that means that if you put in a label in the formaldehyde with O-18, the O-18 will not be seen because you see the oxygen atom of OH^- in the product. Or if you take $^{18}\text{OH}^-$, water, then it will end up in the product. So, we could see that and that was an exciting reaction of course because I like these simple ions.

GRAYSON: [Yes].

NIBBERING: And then we presented that in Vimeiro [Portugal], we had submitted it at the International Journal of Mass Spectrometry and Ion Physics that is in the publication list and John [F.] Paulson from . . . what is that Air Force base lab in . . .

GRAYSON: Oh, Wright? Wright-Patterson [Air Force Base]?

NIBBERING: Let me see . . . Paulson and [Michael] Henschman.

GRAYSON: There is a few trails that operate out of . . .

NIBBERING: Hanscom, the lab that is in air force base, Henschman was from the Brandeis University. Paulson and Henschman and they have seen it in a completely different experiment. But they had published in . . . I have given it here in the reference list. It was an abstract for a meeting. We didn't know that of course. At that time certainly not.

GRAYSON: [Yes].

NIBBERING: And then later on we extended that reaction by making NH_4^- because if you take ammonia you can make NH_2^- in the negative ion mode and if you react with the formaldehyde then it makes in an exothermic reaction in that way. That HCO^- meets another ammonia molecule and transfer then its hydride to ammonia to give a hydride solvated ammonia molecule and that has been studied also by spectroscopy later on.

GRAYSON: Okay.

NIBBERING: So, I like the simple chemistry. Another thing about it, with chemical ionization you could use H_3O^+ and NH_4^+ . So, you could start your lecture and just say, "Oh we'll now talk about the ion-molecule reactions of H_3O^+ , NH_4^+ ," so people thought, "Oh, what's going on? What sort of ions is this—negative ions?" It was H_3O^+ , NH_4^+ now but you had H_3O^- , NH_4^- species. And we made even the radical anion of water. That was work done by Leo de Koning as a PhD student.

I must say if you look up in the literature about $\text{H}_2\dot{\text{O}}^-$ minus radical with a cation of water if you read it very carefully we did of course perform deuterium labeling. We did elemental composition measurements to be sure. It was a reaction [between $\dot{\text{O}}^-$ and] methylamine, ethylamine. It ends up then in a radical anion of water but is not a water molecule

in that structure. We think it is an OH^- with a hydrogen atom and where is the hydrogen atom? I personally think that it is at one of the hydrogen atoms of OH^- .

I have asked Matthias Bickelhaupt some time ago but I don't know whether he has time free to do the calculations. But we wrote, I was very, I've always made doubts doing science. You don't want to make mistakes. But then I have written together with Leo taking all the observations from the experiments together. We are forced to assume that H_2O^- , a radical anion can exist as a stable species in the gas phase.

Well my personal idea about it is if you have a hydrogen atom in the neighborhood of a hydrogen atom in the OH^- always attracting electrons and we know well from my study in the University of Amsterdam the protonated hydrogen is a stable species. And the radical cation of hydrogen . . . I mean you can bind hydrogen with one electron. So if you attract the electrons to the oxygen you get something like an H^+ and then there is an hydrogen atom in the neighborhood, so you can make a H_2 radical cation more or less.

GRAYSON: Crazy.

NIBBERING: I had the correspondence also with groups in the United States about it and they accepted probably that explanation. But I was very, very careful. Dipole stabilized cations I have written from dimethylformamide. You know the molecule of dimethylformamide?

GRAYSON: I'm not very familiar with it personally. [laughter]

NIBBERING: It is $\text{HCON}(\text{CH}_3)_2$ groups. It's a very well-known solvent molecule.

GRAYSON: Okay.

NIBBERING: If you abstract a proton when you make negative ions then you could abstract the proton from the formyl position but that is a minor reaction. You could also abstract a proton from one of the methyl group, because you make then a CH_2^- carbanion ion conjugated to a carbonyl group. So you can delocalize the negative charge.

GRAYSON: Okay.

NIBBERING: Of course you get $\text{CH}_2^- \text{NC}=\text{O}$ and so you can delocalize the negative charge

over the <T: 105 min> amide group—the oxygen. But the funny thing is, these methyl groups are not equivalent in dimethyl formamide.

GRAYSON: They're not?

NIBBERING: No, because one of the methyl group is more or less *syn* to the carbonyl group .

..

GRAYSON: Okay.

NIBBERING: . . . and the other one is in the anti position. And it turns out that the acidity of the anti is higher, is easier to abstract a proton from the anti-methyl group than from the *syn*-methyl group. It is also known from theory. So, the different behavior of the two methyl groups, you see that perfectly from the deuterium labeling. I think that is a highlight also but it confirms that the rotation of the N, around the nitrogen carbon bond is not easy because otherwise you could simply convert *syn* and anti by rotation.

GRAYSON: [Yes].

NIBBERING: [Yes]. But that means that the N-C bond is a double-bond character. And, Mike, that has also been show by gas phase NMR experiments and the rotation is as high, as far as I remember, around 90 kcal per mol, so that is a 3.5 electron volt. So, it is very difficult to rotate and therefore we can see that the anti-methyl is very different from the *syn*-methyl. One exchanges hydrogen atoms, the other one doesn't exchange hydrogen atoms. [laughter]

GRAYSON: Crazy.

NIBBERING: Crazy. Now but chemically it is a very attractive thing. I mentioned already ion emission control in FD [field desorption].

GRAYSON: [Yes].

NIBBERING: I mentioned already field desorption negative ions. I mentioned also the problem with the streetcar in Amsterdam. I think that was also a highlight. I mean, to come up with a solution. Isn't it?

GRAYSON: [Yes].

NIBBERING: I mentioned here also the formation of doubly-charged [negative] ions from a singly-charged negative ion by collision. Strip of an electron from a negative ion. In general I would say the bimolecular chemistry, we did [by use of] FT-ICR. It was a real success. What I also would like to mention is skeletal rearrangements in ions. I like to solve puzzles, you know. But you have to think hard, hey?

And let me, not to go too much in detail but simply show what we did; and the reason we did has to do with phenoxyethyl chloride. If you made the $C_6H_5OCH_2$ ion, that is a phenyl O double-bond CH_2^+ ion that behaved according to their metastable decompositions very complicated. There was a narrow metastable ion [peak] and then broad metastable ion peak, so there were more channels. Then in the end we decided to make anisole, that is a phenyl with a methoxy group, and if you label that with C-13 in the methyl group then what you will see if you generate the $(MH)^+$ ion. [. . .] That ion loses carbon monoxide but it doesn't contain the carbon atom of the methyl group. It contains a carbon atom from the ring.

So, I would like to mention at this point the lab technician, Tineke [A.] Molenaar-Langeveld. [. . .] She was the lab technician, <**T: 110 min**> when I started to become in charge of mass spectrometry during my PhD as I explained. Professor de Boer said "She can work with you, I don't mind." And so, she has worked all the time during my career to make labeled compounds. She was very good in that, minimum quantities. And she learned, of course, to know a lot about mass spectrometry, so you will see she is co-author on many papers.

GRAYSON: Sure.

NIBBERING: So, she did that—she synthesized of the C-13 labeled phenyl methyl ether. Steen Ingemann who was a permanent staff member also in my group like Leo de Koning, he asked me also to help with the interpretation because it was so complex. Now in the end it was successful I must say though I think it is a highlight of what labeling can tell you.

GRAYSON: Oh [yes], sure.

NIBBERING: Well, then I mentioned the [self-constructed] orthogonal time-of-flight [coupled to the ZAB-2HF instrument and the laser for photo-dissociation of ions]. I think that was, in the end, a successful project. The highly-charged noble gas ions, you know, single-electron transfer, double-electron transfer, I think chemically it was also very interesting. I have another one; benzonitrile. Tineke also labeled it with C-13 in the cyano group and now you look at the meta-

stable [molecular] ions. [They eliminate] HCN, hydrogen cyanide. [That molecule] contains only 7 percent C-13. But she put a label in the cyano group. So 93 percent is coming from the ring. Well you have to read the paper, how we do that. You have a complex skeletal rearrangement of course.

GRAYSON: Ah, [yes].

NIBBERING: But what is the interesting thing? The benzonitrile was a compound which was used to test RRKM [Rice–Ramsperger–Kassel–Marcus] calculations. [laughter] There they said the HCN loss was a 1, 2-elimination from the aromatic ring making benzene, but now you see it is complicated. There's a skeletal rearrangement going on. [laughter]

GRAYSON: I'm not sure how that happens.

NIBBERING: [laughter]

GRAYSON: Pretty impressive.

NIBBERING: It's pretty impressive. I think [also about] the phenonium ion formation work I did in Fred McLafferty's lab . . . you know, the Brown-Winstein problem?

GRAYSON: Okay.

NIBBERING: They had the phenonium ion, but later on we made also its negative analagon. So it's easy you can delocalize the charge over the ring in a phenonium ion but you can do that also with a negative charge, so we made a negative analagon.

Then field ionization kinetics, I think what was a very nice observation is the following and it was done on the ZAB instrument and it was always a wish of me. We had studied [before with the use of the Varian MAT machine] pentenols also in cooperation with Alex Harrison from the [University of] Toronto; one of my students, Jan [J.] Zwinselman, he moved [after his PhD study as postdoc to Alex Harrison. But if you look at the phenomenological rate constant [by use of the ZAB instrument] then we found in the phenomenological rate constant [for methyl radical loss] two maxima; one at around 10^{-11} seconds decomposition and one at around 10^{-10} , and that was due to the high resolution of the electric sector of the ZAB that we could separate the maxima which we could not do with the Varian MAT machine. And what you can do now, you can select the maximum so that is to say you select the ions with a lifetime of 10^{-11}

seconds and you do collisional activation <T: 115 min> on these ions to get their structure. Now you shift to the one at 10^{-10} , during collisional activation there is another structure and we know the chemistry, so we could prove the structures by time-resolved MS/MS. And I think it is a really unique example in the mass spectrometry literature. I wish that we had more of these examples but . . .

GRAYSON: [Yes], they're pretty interesting.

NIBBERING: But it works *only*, Mike, if the ion at 10^{-11} seconds is not rearranging any more during its flight. And the same holds of course at 10^{-10} [seconds] so there are conditions, which have to be fulfilled, but I think it was a nice experiment; time-resolved MS/MS.

Then I mentioned already the use of the ZAB instrument as a laboratory on its own. [Make the] methoxy, convert it into the methoxy cation, and select it, purify it, and then do reactions. What I also like to mention is infrared assisted field ionization kinetics . . .

GRAYSON: Oh wow.

NIBBERING: . . . because, field ionization kinetics, you can only see a primary fragmentation reaction of the molecular ion. Field ionization is a soft ionization method.

GRAYSON: Right.

NIBBERING: And so sometimes you simply don't see a fragmentation and so you cannot study time-resolved reactions. Then you could say is that important? That is the game that we like to see these reactions—that is the science. And Ilse Aben whom I mentioned before, she had studied physics at the Vrije Universiteit and was used to lasers. I said, "Ilse, let us look at the use of infrared laser to warm up, vibrationally excite, the molecules before they are field ionized, and look whether we can de fragment [the molecular] ions." That worked well. It worked. It's nice.

I'm almost at the end here. Acidities of radicals. If you take methane it is not acidic.

GRAYSON: Right, right.

NIBBERING: If you take methane [it requires much energy to split into the methyl anion and a proton]. If you take a methyl radical, that's possible. The methyl radical is more acidic than

methane. If you take methyl chloride, you can abstract a proton from it so it is acidic, but if you take the $\dot{\text{C}}\text{H}_2\text{Cl}$ radical, that's more acidic than the chloromethane. So we have found by—you have to play with thermo chemical cycles, of course, to do it—but we found in general that radicals from these kind of compounds are more acidic than their parent compounds.

GRAYSON: Okay.

NIBBERING: And if you look in atmospheric chemistry there certainly will be radicals. And if you incorporate these kind of things in schemes—reaction schemes—then I think it is a nice observation that we have established that they are more acidic, that you have to take into account. Most of the time you think radicals are very reactive but not in the way that they can act as acids. [Recently I had an interesting] paper together with Veronica Bierbaum.²⁹

GRAYSON: Okay, Veronica.

NIBBERING: Veronica . . . [yes], we called her always, Ronnie, her nickname. I've known her since I was in 1980 of course in Boulder, Colorado, with Chuck DePuy. She asked me, I think, last or the year before. She was guest editor for an issue of the *International Journal of Mass Spectrometry* to celebrate the sixty-fifth birthday of Peter [B.] Armentrout. And so Ronnie asked me, can I contribute a paper? <T: 120 min> And I would like to contribute the paper, of course, to Peter Armentrout. I wrote to Ronnie, "Ronnie, I have no instrumentation anymore, and I have no group anymore, but most important I have no instrumentation."

Then she said, "Well if you propose a project, we can do the measurements." And then I thought about the following: we always did negative ion-molecule reactions and using frequently the radical anion of oxygen, making from N_2O . If you fire low energy electrons on N_2O you make O^- —radical anion of oxygen by elimination of N_2 —and then you can do all kind of reactions with organic molecules. And having been in Boulder and knowing that they are doing atmospheric chemistry, I thought, well, let us look at the radical cation of oxygen and later to react with a simple compound like methyl chloride, methyl fluoride, tetrafluoromethane, methyl bromide, methyl iodide, et cetera. And so she did the experiment with the flowing afterglow, with the help of students of course and in the end it was a nice thing because the radical cation of the oxygen atom is in its ground state a quartet.

If you have the atomic orbitals of oxygen, if you look at that and that is logical that it is a quartet because Hund's rule says you have three electrons in p-orbitals, Hund's rule says you should have them in different orbitals [. . .]. That's the lowest energy, so therefore a quartet. But

²⁹ Nichols, Charles M., Zhibo Yang, Benjamin B. Worker, Denver R. Hager, Nico MM Nibbering, and Veronica M. Bierbaum. "Gas-phase reactions of the atomic oxygen radical cation with halogenated compounds." *Physical Chemistry Chemical Physics* 15, no. 2 (2013): 561-567.

then if you react this ion with the methylhalides then, if the oxygen atom would stay in the quartet state [the reaction] is impossible because the reactions will be endothermic. They cannot occur. So, during the formation of the ion-molecule [complex] at some stage of the reaction is a spin flop. That means the spin is inversed. You go over from a quartet to a doublet and that has not been considered so much in the ion-molecule chemistry field.

GRAYSON: Okay.

NIBBERING: Ronnie will say it is not unknown, but it has not been considered in our field of ion-molecule chemistry. So, I was very happy with that. That is in the list of publications at the end of what I sent you. And that was a successful, a highlight.

GRAYSON: Well those were the ones that we want to get. And we just want a chance to make sure that we get them right and . . .

NIBBERING: [Yes], sure. Then I would like . . . about FT-ICR—the homemade FT-ICR—I would like to mention the notch ejection technique. [. . .]

[recording paused]

GRAYSON: Okay, let me make sure that we're still okay.

NIBBERING: The notch ejection technique on the homemade FT-ICR. Because that is the thing where you scan to eject ions from the cell. You scan the frequency and suddenly the ions you would like to keep in the cell, they will shift the phase of the pulse 180 degrees and then continue. And then at the point where you change the phase 180 degrees, these ions will stay in the cell. And that was developed by Andre Noest and Jim Dawson. And we used that over all the years in the homemade FT-ICR. Well a colleague sometimes said you should have done more work on it because later on, SWIFT, was developed by Alan Marshall. That went over very well. But I think it is a nice method to isolate ions in a relatively simple way in the cell.

GRAYSON: [Yes].

NIBBERING: It was not high resolution selection, but it worked for our ion-molecule chemistry perfectly.

GRAYSON: <T: 125 min> Let's see, I don't know how we're doing here. I guess a good question at this point—we're, kind of, getting toward the end of the major topics here. What do you think is the impact of your research on the field of mass spectrometry over your career?

NIBBERING: It's a difficult question.

GRAYSON: You've conducted research in so many different areas in both the theoretical fundamentals of thermodynamics and ion-molecule reactions but then you've done a lot of instrumental . . .

NIBBERING: I think, Mike, that other people would say that, fundamental gas phase ion chemistry, both unimolecularly and bimolecularly but especially mechanisms.

GRAYSON: Okay.

NIBBERING: Because you know . . . why do I have such a question? First we were always interested to look how it exactly happened—driven by curiosity. But many other people have worked in that field. So, what is my contribution and not only me but from my group, the co-workers, et cetera? Well, I notice that many people appreciated what we have done. I mean, when I was in West Lafayette, [Indiana], this weekend, Purdue, the people said that, “A sense of contributions.” And that is a pleasure to hear and they were honest, I think. But did I do the work that people could use it or found it interesting? That's difficult to predict.

GRAYSON: Okay, but I mean the fundamental studies I think are important.

NIBBERING: They are important.

GRAYSON: I mean because they do . . .

NIBBERING: That is something that I will be on that line, so if people will say, “What is the use of fundamental research?” Then I [would say] very . . . fundamental research is essential to get to innovations. But most of the time the work, what you do, you cannot predict whether it will be useful or [not] . . . many years later.

GRAYSON: Okay.

NIBBERING: I mean, if I come back again to the Purdue University, they use chemistry there to get the best results from, for example, the paper spray work. Then I say, “I see then the usefulness of it.” Okay, could I have predicted that? No, no, I was in – . . .

GRAYSON: [Yes].

NIBBERING: No, no, no. I am a member of the Royal Netherlands [Academy of] Arts and Sciences, so we have many times these discussions, because it has to be relevant for the society and innovative, et cetera. But there are older colleagues in the Academy who say you never can predict whether it’ll be useful or not. That is not a driving force. If you could predict it then you don’t have to do the experiments anymore.

GRAYSON: [Yes], right.

NIBBERING: [laughter] It’s as simple as that.

GRAYSON: Well, I think we’ve covered pretty much your career in the things that I wanted to talk about. I don’t know if you have any other comments to make at this time and, if not, we can take a break and think about doing the video?

NIBBERING: I think we have covered more or less the exploration and background for interest in . . . yes. Now, the discussion on the field of mass spectrometry. Oh, I would like, of course, to mention that we have a list of names of research colleagues. Steen Ingemann, he was a permanent staff member with a group in the end, Leo de Koning, they both got their PhD with me [. . .] Susumu Tajima. He was a visiting scientist in 1977 and I still have very good contact with Susumu. He became professor of physical chemistry. <T: 130 min> Jan Kleingeld I have mentioned. Jan van der Greef, [who became professor of bioanalytical mass spectroscopy]. Matthias Bickelhaupt, [who became professor of theoretical organic chemistry]. Helmut Schwarz, Monique Born was a lady who did the acidities of radicals and heats of formation of carbenes. Albert [J. R.] Heck, he did also very basic research in my group but then after having postdoc’ed in the United States he came back and became Professor of Biological Mass Spectrometry at the University of Utrecht. And he is at present the Director of the Netherlands Center for Proteomics.

GRAYSON: Oh, okay.

NIBBERING: [Yes]? Satoshi Nakajima, that was a co-worker of Susumu Tajima. We worked at the end of my career when I was a guest after my [early retirement from the University of Amsterdam at] the Vrije Universiteit I still had cooperation with Susumu Tajima on silicon-containing ions.

GRAYSON: Oh, okay.

NIBBERING: That had to do with the silicon industry. Frans Pinkse, I mentioned.

GRAYSON: [Yes].

NIBBERING: Wim van der Hart. That is the ultraviolet photodissociation work at the University of Leiden.

GRAYSON: Okay.

NIBBERING: So when I said phenoxyethyl chloride, the final experiment which solved that it was a cyclohexadienone, the keto structure of phenol, that was done with Wim van der Hart with whom I had a very good relationship but he was at the University of Leiden and I even thought perhaps he could join my group. He was at group meetings in my group. And then Noll Venema he is on the list. He did very good work in the beginning of my career, PhD student, but then went to industry. He was a student who came late in his career that he started to study at the university. And then so he had a high technical school education, but it allowed him to enter the university and Noll, after his PhD was an extremely good PhD student then he joined AkzoNobel in Arnhem [Netherlands]. He became part-time professor in analytical chemistry in Ghent, Belgium, but unfortunately he passed away because of pancreas cancer.

GRAYSON: Oh, no.

NIBBERING: [Yes]. Too young. Absolutely too young.

GRAYSON: That's one of the worst ones.

NIBBERING: [Yes], it's one of the worst ones. Then you see on top of the research colleagues there is Roel [H.] Fokkens . . .

GRAYSON: Yes.

NIBBERING: Roel Fokkens, that is the man with *Fingerspitzengefühl*.

GRAYSON: Okay.

NIBBERING: He was originally a lab technician. He could operate all kind of different instruments. I said to Roel, please try to do it as long as you can.

GRAYSON: [laughter]

NIBBERING: But Roel had an education. Not an academic training, but like Noll Venema, that allowed him to go up for a PhD, an academic degree at the university, so his pre-schooling was such that it's possible. And he worked for many years with me and we had many other scientists coming worldwide to our group, to our institute, and so Roel is also on many papers co-author. And the scientists who were in my group from outside the Netherlands, they said he's a very capable man. Then when I got more or less in the stage for the early retirement because of reorganization there, I will not bother you with it, but then I said to Roel, "Roel if you would like to stay at the University and we'll get a good position then at least you should have your PhD," and that was possible for him and I contacted also the scientist in the world with whom he did the measurements and studies and they fully agreed. So then I said, "Roel, but I cannot be your supervisor," because we are too much connected with each other.

GRAYSON: Sure.

NIBBERING: And so I asked Jan van der Greef who received his PhD with me, "Jan, would you like to act as the promoter, so to speak for <T: 135 min> Roel Fokkens to get his PhD at the University of Leiden?" And so it worked out. Then he moved from the University of Amsterdam to the University of Twente to work in the group of David Reinhoudt. By the way, that instrument which we had that was David's instrument, you know, we moved that back to the University of Twente. I didn't have to move but he took it back and they were very upset at the University of Amsterdam; but that was the deal.

Because David said to me, “If you are not there anymore then I will take the instrument back to Twente,” and Roel started to operate with that instrument. There was already other instrumentation and he built up also their mass spectrometry. But then at a certain point in time he decided to join industry and he went to a pharmaceutical company in Nijmegen called Synthon, because perhaps also in the United States that pharmaceutical companies, some of them are in the Netherlands. Organon was a pharmaceutical company taken over by Merck and Merck was more centralizing but Synthon came out of an organic chemist from University of Nijmegen who started that company. [. . .] Synthon [is very] successful and the Roel became head of the analytical division. I have regular contact with him. He has now three hundred fifty employees.

GRAYSON: Whoa.

NIBBERING: The analytical department, because they have also branches of that company here in the United States, Chapel Hill, North Carolina, but also in Argentina, in Spain, in the Czech Republic, in Australia. So it was very successful. For me it’s also a pleasure to see, Roel did very well not only at a university but also in industry.

GRAYSON: For them it’s great.

NIBBERING: [Yes].

GRAYSON: I see it’s interesting you have all these collaborations. You have papers with so many other co-authors all over the world. A lot of America.

NIBBERING: [Yes].

GRAYSON: Some in England, some in Europe, and I guess your initial travel, on the Royal Dutch Shell got you interested in collaborating with people around the world.

NIBBERING: Yes, that is one thing but I think also my character is in that way . . . really.

GRAYSON: I think so. [laughter]

NIBBERING: Because I never forgot, of course, to do my own research. Because if you are all the time doing measurements for other people, then people will say, “He’s like an . . . well, a lab technician?” I want to do my own research and then also instrumental developments. I have driven motorbikes so that helps also that you are interested in instruments. But I liked also to do the applications, which was also a necessity to get money. I mean it’s difficult in a chemistry department to say, “I would like to have an instrument,” *and then* do only my own research.

The instruments were at that time too expensive. It’s completely different for physicists. They built an instrument and then they do their PhD, they run only themselves, that instrument and nobody else. That was not the case in our case and so therefore John Bowie who was in Amsterdam. He was surprised to see how analytical service was mixing with research. So one day we did that, next day it was completely pure research and then again applications but the applications gave us also the opportunity to learn about other fields, isn’t it?

GRAYSON: Sure. And get those interactions that you wouldn’t get any other way.

NIBBERING: [Yes], sure.

GRAYSON: So I don’t know. Is there anything else? We’ve talked about all these people and about their . . .

NIBBERING: I think so. I see the name of Dom [Dominic M.] Desiderio. I’m doing the book series of Wiley with him, because Dom and I were the co-editors of *Mass Spectrometry Review*.³⁰ Originally that was done with Maurice [M.] Bursley but Maurice had then I think some health problems or for temporarily and then I continued to keep the journal alive and then you know the system is different in Europe than in the United States, so it was really difficult for me. I managed <T: 140 min> and then Dom was in the picture to become co-editor, and so he found me and he had informed about myself, my person, how I was, and that was a very good combination. But then in 2001, the first of October, I officially had to retire with an early retirement because of reorganizations. But I said to Dom then in 2000, already, I cannot continue that without a secretary. But then Dom said we have had such a nice cooperation over all the years and I said, “Okay,” and he said, “Could you help me with the book series.” Then I checked with him how much work it would be and he said, “Okay, I will do the book series.” And then we discussed of course the *Mass Spectrometry Review* journal and, well, Dom is now editor-in-chief. That was decided also then and my opinion is you should have somebody in the fundamental part, one for instrumentation and one for the application.

³⁰ Nibbering and Desiderio are series editors for the Wiley-Interscience Series on Mass Spectrometry. For more information see: <http://www.wiley.com/WileyCDA/Section/id-390722.html>

GRAYSON: Okay.

NIBBERING: And at the moment it is Einar Uggerud and Paul Vouros and Carlito [B.] Lebrilla. But in the beginning we have Michael Guilhaus from Australia, because I said also to Dom *Mass Spectrometry Review* that journal. Well, that's my opinion about mass spectrometry anyhow, but it should be worldwide, so don't put only Americans in the editorship. I mean take editors also from other parts of the world. It's better.

GRAYSON: Exactly.

NIBBERING: And it worked out also, well except that Michael Guilhaus passed away too early also because of cancer problems.

Now with Graham I had cooperation already in the beginning of my career, 1974. He came along and I worked on a problem and he said, "I could help you." He was nice and since that time we always kept contact. We did angle resolved mass spectrometry with him to compare it with field ionization kinetics. Now Fred you know; John Beynon, when he was at Purdue we had already cooperation; Mike Gross is known.

GRAYSON: Oh [yes].

NIBBERING: Peter Derrick in field ionization kinetics. Keith Jennings, because of collisional activation studies. He was the man from the collision-induced dissociation. Mike Bowers, Mike is a physical chemist, and I like Mike very much, and we did also editing and special issues for Keith Jennings; but I have never had a paper with Mike Bowers. We did the special issue for Keith Jennings but I think it is a very good colleague and he informed me also about what was going on in his lab and he asked my opinion about it and, no, a wonderful colleague. Now Richard [M.] Caprioli, well, he is the editor in chief of the *Encyclopedia of Mass Spectrometry* together with Michael and Richard also tried to get me as editor-in-chief for the *Journal of Mass Spectrometry*, if I remember correctly but Peter was editor-in-chief for the *Organic Mass Spectrometry* journal and Richard was the *Biomedical Mass Spectrometry* journal. And I tried to keep Peter in the business, but, you know, that didn't work out, but I didn't want to be unfair with respect to Peter, and so I said, "I can only be a regional editor, not more." Although whether Peter understood at that time, I don't know. Well, okay, that doesn't matter. There are sometimes things that happen in your career which you say, well, you cannot avoid everything.

GRAYSON: [Yes].

NIBBERING: Emilio Gelpi, he was one of the first founding members of the International Mass Spectrometry Society. At least we were the first members of the international mass spectrometry board I would say. Graham was president, Emilio was vice-president, I was treasurer. John [K.] MacLeod from Australia, you can find it in the literature of course. He was a member. Graham asked me also to think about people from other sites outside Europe because the international mass spectrometer conference started in Europe and were always held in Europe.

GRAYSON: Right, right.

NIBBERING: So I divided the world in three regions. There was region A, Europe. Region B was Southeast Asia and Japan, and Region C was America and South Americas, <T: 145 min> Canada. We had representatives from these parts and I was chairman of the Twelfth International Mass Spectrometry Conference in Amsterdam in '91. [Fig. 8] And in organizing that because the bid was accepted in Swansea [United Kingdom], the tenth was always six years before and, well, I had a team around me that worked perfectly. Piet Kistemaker and other people and I myself was also for the science.



Figure 8. Nico Nibbering at the Twelfth International Mass Spectrometry Conference in Amsterdam.

I got the congratulations from many people that it was a very well-organized conference, very successful, but there were financial problems. The exhibition saved us, I can say to you because if you would have lived on the participants then it . . . no, negative. But we split our budgets for the exhibition and then said to [. . .] get so much percentage of the exhibition and

that saved us. But then I discussed, I remember with John Beynon and with Graham Cooks, I said to them, “I don’t understand why money which is left over if it is left over from a previous conference cannot be used for other upcoming conferences?” [. . .] Because the physicists did it; that I knew. [Fig. 9 and 10]



Figure 9. John Beynon at the Twelfth International Mass Spectrometry Conference in Amsterdam.

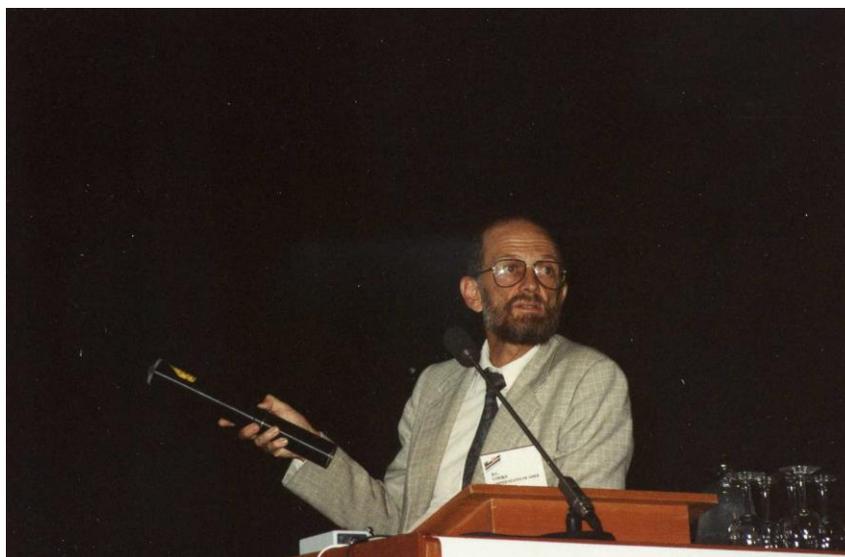


Figure 10. Graham Cooks at the Twelfth International Mass Spectrometry Conference in Amsterdam.

GRAYSON: [Yes].

NIBBERING: And I think that was picked up, that idea more and more by Graham also and John Beynon. I think also that is a logical thing.

GRAYSON: So what would happen to the money? In other words, at the end of the conference there is money left over. What do you do with it? Do you give it back to the people? I mean do you give a percentage back to the people at the end?

NIBBERING: No, no, the thing was that we said we are not aiming to make profit.

GRAYSON: Right.

NIBBERING: That's not the way.

GRAYSON: [Yes].

NIBBERING: But if money is left then it should be used only for promotion of mass spectrometry. That was a problem because in Amsterdam or in the Netherlands we were part . . . what was mass spectrometry it was a discussion group . . . under the umbrella of analytical chemistry, under the umbrella of the Royal Netherlands Society for Chemistry. But then when we had the bid for '91 in Amsterdam decided by the International Committee in Swansea then I got in touch with the Royal Dutch Chemical Society and I said, "We would like to organize a conference because that has been approved." Okay, and they said, "[Yes]," "But the money which would be left over, that should be used only for mass spectrometry." Oh, they were very angry; but I thought, well, the mass spectrometrists, they decide for their field, isn't it? So, then that ended up in the Dutch Society for Mass Spectrometry and to the Netherlands Society for Mass Spectrometry. Of course the discussion group was founded in twenty-sixth of February in 1964. I did my master's degree, so I remember that meeting.

GRAYSON: Okay. [laughter]

NIBBERING: There was an existing body for mass spectrometry, but it was not a society, but that was transformed into a society because of the '91 meeting. I said, also, to the chemistry it took seven meetings to get it done because chemistry . . . I said, "It is not only chemistry, it is also physics." So it should be under the umbrella also of the physical, the Netherlands Physical Society and that was accepted. We were an independent society but under the umbrella of the physics society and the chemical society.

And then money left. We made a scheme also. Graham helped of course because you could copy that a little bit from the ASMS. If money is left then a certain percentage is transferred to the next conference.

GRAYSON: Okay.

NIBBERING: But I don't know how it's at the moment working because so many years ago that it changes over time. But now you see also how the connections are with Graham <**T: 150 min**> and with John Beynon, et cetera. I see Brian [N.] Green with Emilio Gelpi, of course. I see Brian Green . . . wonderful man.

GRAYSON: [laughter] Crazy guy.

NIBBERING: But wonderful. You know, the VG Micromass decision, to make that instrument contrary to a MAT machine; because that good it's really with [VG Micromass], you came with your samples and asked to run of course the spectra and asked for all kind of experiments. And Brian was always in favor of it. I said, "Brian, can you do it?"

"Oh [yes]."

GRAYSON: [laughter]

NIBBERING: And it was an excellent demonstration; and I liked the way in which he worked. Brian is [makes kissing sound] perfect. He is still going to the lab.

GRAYSON: Really?

NIBBERING: [Yes], he smokes, still, a lot. Like on the flute. [laughter]

GRAYSON: Oh okay, like a chimney. [laughter]

NIBBERING: Alex Harrison, I met him, of course, in the first trip to the United States, that was last when I visited, in '69. There is a Dutchman who got also his PhD before I was in mass spectrometry. That was Feie Meier.

GRAYSON: Oh [yes].

NIBBERING: He became a very important director at Philips. So, there was the connection with the Netherlands also and later on Jan Zwinselman spent his postdoc with Alex. So, I know Alex for that reason also for many years. Carlito Lebrilla, he came over to Amsterdam. He was in the group of Helmut Schwarz to do experiments on the sulfur stuff with Asmus, et cetera. Sy Meyerson, well, I mentioned I met him during my trip through the United States in '69 and I visited him. [Fig. 11] But we had also from this paper, we looked at what he had done in propionitrile and then Carla Theissling was in my group and we did experiment and I said that's important for Sy Meyerson to know. So, we informed him, we sent him the manuscript, and he made some comments and said, "Sy is the co-author."³¹

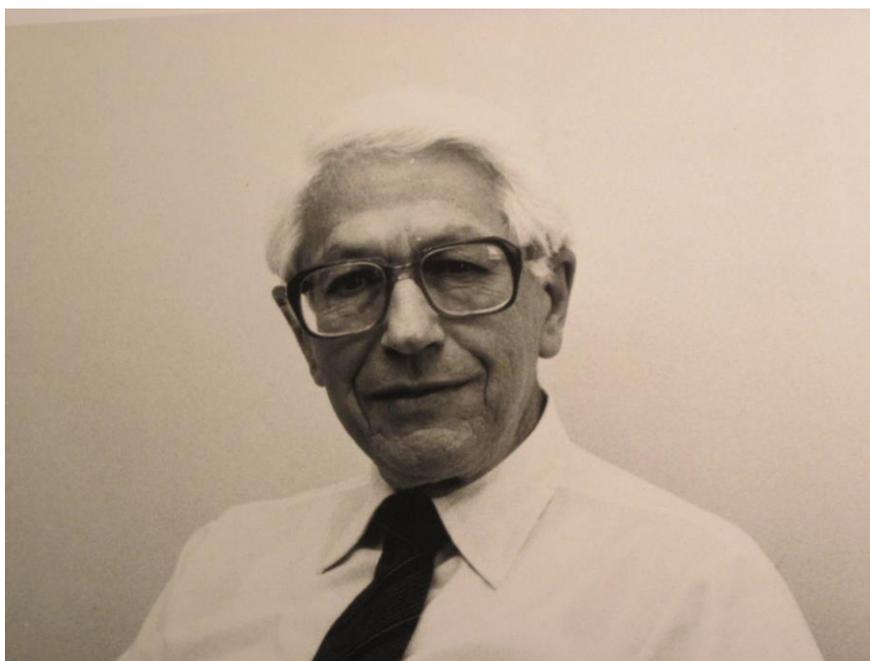


Figure 11. Seymour Meyerson

GRAYSON: Nice.

NIBBERING: Simple as that?

Michael came over frequently to Amsterdam because we went on holidays but he was also in the lab and at that time we had compounds, endorphins from [. . .] a pharmaceutical

³¹ Carla B. Theissling, Nico M.M. Nibbering and Seymour Meyerson, "The long-lived molecular ion of propionitrile: an ion cyclotron resonance study." *Org. Mass Spectrom.* 11, 838-843 (1976).

company; also peptides, ACTH [adrenocorticotrophic hormone] peptides. And I informed Michael about it and he said, "Oh, I'm interested, can I get also these compounds?" You know, these compounds were released from the company when it was not critical, of course. So we could do the experiments to compare the collisional activation spectra on our ZAB machine and compare that with the Kratos triple sector instrument of Michael. And so that was a very useful collaboration in this hardware project we had with Michael, but which instrument was better then? We have our differences.

GRAYSON: Oh [yes].

NIBBERING: And John Bowie, John Bowie came when he made the trip to England I think somewhere in the mid-70s, and came along and he did see that we had a book on negative ions from Ardenne. And he felt it was interesting. I don't say that John is smart enough and knows exactly what he has to do; but he moved into negative ions and I visited him a number of times and I had cooperation with him sometimes and even after my retirement he had a question about a thing and then I proposed something and he said, "You should be co-author." So John is a nice colleague and a real physical organic chemist.

GRAYSON: Well, we've gone through those collaborations that are outside of your immediate area. We talked about your publications, about the most significant ones.

NIBBERING: At least as far as I see it?

GRAYSON: Well, that's much better just on the questions part and so I think we've pretty much covered everything.

NIBBERING: I think so.

GRAYSON: I guess there's one thing I did want to touch base on. Maybe we'll cover that. I'd like to do the video too but why don't we take a break and have some chow.

NIBBERING: [Yes].

GRAYSON: And then we can do the video and I'll ask to have the video on.

NIBBERING: I see, “Match your careers, significant issues affecting your career direction, where you have had good events, bad events.” Well, the bad events . . . I mean you can imagine <T: 155 min> if there is a reorganization then mechanisms become into operation which are in my opinion not always rational. There are more things to it.

It gets . . . other considerations begin to take precedent.

NIBBERING: Exactly, yes, but fortunately the Vrije Universiteit, because I have a good contact with there also for the analysis stuff which I did for them. They also said we will not go in to do research in mass spectrometry but they had equipment to analyze but not all the instruments, so they came to us like other universities and so therefore they said when they noticed the problem of early retirement, “Why don’t you come here as a guest?” So, during my sabbatical I traveled a lot. But on the first of October 2000 I went there already, got a room and worked on the *Encyclopedia of Mass Spectrometry*, participated in the group meetings of Steven Stolte, physicist from origin but in physical chemistry.³² One of his students got his PhD with me, so you know then how the interaction was, Steven Stolte is still a very good colleague.

GRAYSON: Okay. I think I’ll push the stop record button.

[END OF AUDIO, FILE 2.2]

NIBBERING: . . . aunt and uncle with whom I grew up to go to high school, which was in *gymnasium* in Zaanlands Lyceum. After elementary school I went to the third school after examination and then the *conrector* of the *gymnasium* division thought that I could do *gymnasium* and I would like to do that. Also my aunt and uncle, they were happy with that, and so I did *gymnasium*, and then during the *gymnasium* I had very good teachers there. One of them was Simons, my teacher Simons. He was a very good man in mathematics, physics, and gave exciting teaching there. And also teacher Mensink who taught us chemistry in addition to other teachers of course but these were the two who, well gave me the idea I should do science. So I made a choice for the *gymnasium* beta and then after six years you do your final examination, and the director of the Zaanlands Lyceum came in and said that you could get forms to apply for grants to study at the University of Amsterdam.

And so I did and the headmaster but also the teacher were instrumental to lead me in the direction of studying chemistry at the University of Amsterdam. And then, of course, I started there and then I followed the lectures of the professors there and one of them was Professor

³² Burgers, P. C., J. K. Terlouw, and N. M. M. Nibbering. *Encyclopedia of Mass Spectrometry*, vol. 4, Elsevier. (2005): 173.

Gerrit Jan Hoijsink and he gave exciting lectures about chemical bonding and I thought I will do physical chemistry. But then he said it is nice to do theory but never forget the experiment and if you do theory sometimes you cannot get your hand on molecules you'd like to study and then I thought, "I have to mix physical chemistry and organic chemistry," and therefore I took the direction of physical organic chemistry with Professor Thymen de Boer, a very good colleague, by the way of Professor Chuck DePuys of the University of Colorado in Boulder.

Then I started with my master's degree, I asked for a subject of course which would be a combination of theory and experiment, and a week later I had to come back to the office of Professor de Boer and then he gave me the subject of mass spectrometry. I didn't know about that field but he asked me to work on a project to show that the McLafferty rearrangement, known at that time for ketones, esters, acids, et cetera, but to show that was also working for 1-nitropropane.

So, I started my practical work there but had to label the 1-nitropropane in the different positions and then using the single-focusing mass spectrometer. The mass spectra were recorded and then from the labeling you could conclude that the McLafferty rearrangement was a detour for 1-nitropropane. Then I thought to go into industry. Either Philips or Shell was logical at that time but Professor de Boer said, "No, no, you could do a PhD with me." So that I did and he said, "Well if you look at 1-nitropropane you replace one of the hydrogens by an aromatic ring and then you can study a lot."

You had to synthesize again these compounds and weigh them and the fact that I got also all the intermediates that made it an extensive study for a PhD thesis. And then during my PhD my predecessor left, went to industry and then staff members started to convince me that I should apply for that job. But I had already interviews with Philips and Shell, and at that time I would have chosen Philips but after they have convinced me to apply for the job it took three weeks but in the end they managed to convince me. I applied for the job with Professor de Boer and Professor Huisman who were the director and co-director. They inter-changed position every two years and they were very happy that I was there, and they asked me, "What do you think about how to do it for mass spectrometry." Of course the intention of them was that I would take care of **<T: 05 min>** the analysis of organic compounds by mass spectrometry and then I said, "If you would like to do high-qualified analysis you need to do research and how do you see that then?" Well I said I thought that you need then a group of at least three because these two ones . . . oh, they said that can be arranged. Although I became head of the mass spectrometer division—but didn't have my PhD at that time—I already got from the message we will get a group with PhD students and that way my career at the university started.

GRAYSON: Well I'm not sure that it's a path that a lot of people would follow but you can give some generalized advice to younger people who want to get into sciences. So what would a young person who is interested in science . . . how would you suggest that they approach the subject or how would you suggest that they go ahead and develop their interest in science and becoming a scientist?

NIBBERING: I think if you are interested to do science then do it and don't think about is it useful to go in that field of science, do I get a job in industry or at the university. Simply do it, what you want. That holds for any subject. And then of course depending on [. . .] going to a university and taking courses there and going to lectures then you will find the most interesting things in which you would like to work further. And so do your best, never think about what the future will bring, and you will become then qualified in the end. I dare to say that if you are enthusiastic, that's the most important thing that in the end you will always find a job that suits you, perhaps not in the field in which you will do your master's degree or PhD study but the most important thing is that you have done something you like to do and you get by this also a very good academic training. That is my experience. So, I always said also to my PhD students if you would like to go in mass spectrometry is okay but sometimes that is not possible at that moment. But you are equipped enough with an academic training that you can also do other things.

GRAYSON: So, this kind of leads into another topic that I wanted to talk briefly with you about and that is about mentoring. You obviously mentored in your career and I think you discussed with us already those events that led you to develop into the scientific field but what are your thoughts about how to mentor other people? You've obviously had a large number of students work for you and postdocs. What kind of guiding rules did you use when you were mentoring these younger people?

NIBBERING: Let me first say that there were PhD students who did their master's degree and then came to me for PhD. The first question was to them, "Do you have a project in mind?" If they would have a project in mind that would be nice then because that is their own ideas and then it would be very good for them to work on that. I can mention one of them like Noll Venema but he was an older student. He had a training which was not that he could easily go to a university but so he entered a university at a later stage of his life. He was not old but at least so experienced that he could say, "I would like to do this and that."

So, then it is easy and then of course you look at your own experience, whether that is a useful approach but I think they said, "We have no idea." Then you gave a project and then I said, "[Yes], the best thing is to start their project by first to going to the library, find out what is known. Because then you can set up things how to do the project and many times they came back and then said, "We cannot find much about this." I said, "Ah!" That is also the reason why I have thought about this so now [. . .] you have to come up now, how would you like to perform that project?" Do you have ideas, planning, et cetera, what is the best method? And of course I am <T: 10 min> available to give advice but please think also yourself, and that worked out quite well because I think you should not guide them that everything is planned by you, the supervisor, you know. They should plan themselves and find out themselves that they can lead to successful results.

Of course I have had PhD students that you could see after two months there was no progress, it was difficult. Now I am not unhappy when there are difficulties because you will also have that later in your life. But so I would say a few months fighting with the problem, no problem at all. But at a certain point in time you have to change, otherwise it will stick and so in that way you would try to help. And it has worked out quite successfully and I must say also the PhD students which were very good in my case which I had all have made it but not all of them in mass spectrometry. That's also not a problem because I said you have an academic training now so you can do a lot of things. By the way, is it the things to be useful at what you do, I always said the fact that we have an academic training, that is already important for the society.

GRAYSON: So, you have been interacting with a large number of your peers in the field. Obviously I think there's some competition involved in different groups working on, kind of, the same problem, trying to beat the other one to getting their answer. What do you think about competition in science? Do you think it's a good thing?

NIBBERING: Competition is good but it should not be an . . . let's say an unproductive competition. I mean, it can be a competition that . . . well to beat . . . of course you would like to be the first but it's not always possible, so you have to accept that. But I think competition means that you would like to speed up your research and get results? But also sometimes we found out that others were working on the same subject and then we said, "Why don't we cooperate?" Instead of fighting and well . . . at least not fighting of course but to have such a competition, so I have had also many cooperation because of that, finding out what the other did in a friendly way we made progress in a way. Of course that is what is important in science, isn't it?

GRAYSON: Progress.

NIBBERING: Progress.

GRAYSON: During your career I think you had the opportunity to interact with a number of women in the field either as students or also as equals in other laboratories around the world. So what is your opinion or thought about the place of women in science?

NIBBERING: I must say that I have been in a very fortunate position that I have had many female PhD students and I think that's first important for science, but also for, let's say, in the industrial world. So, in addition to the academic world it should not be only a man-business, not on that line.

GRAYSON: Okay.

NIBBERING: Not on that line. Because also I can say female persons, they bring in additional things how men are operating and I think sometimes the creativity of women is very good. And they are also more precise if I look at the interpretation of mass spectra. Men do it in a . . . well, sloppy way sometimes. Well they are more precise. That I have experienced during my career.

GRAYSON: You've had a fairly long career in the field. What do you see the largest, most important changes in the field of mass spectrometry over your career?

NIBBERING: The largest change is that it started in physics and chemistry, of course. Physics remains a very important part of mass spectrometry because of development of instrumentation. Methodologies. Chemistry remains very important to understand what is going on in the mass spectrometer <T: 15 min> collision activation experiments or other kind of experiments. We will observe, well, signals in the mass spectra that you have to think about. I am not against databases if you can use that, yes, but in the end there are frequently occasions where you have to use your brains to get to understanding of what is going on.

And the changes, of course, [. . .] well it started in physics, so they came into chemistry and now it is more in the biochemical field, medical field, life science as they call it. I think that is a very good thing for mass spectrometry. But also realizing chemistry, the molecules which are studied are supramolecular systems—so very large systems held together by noncovalent interactions. I've been a guest professor officially for four years at the University of Twente with Professor [David N. Reinhoudt,], a colleague of mine. They were working on supramolecular assemblies and these systems are also very important for microelectronics, optoelectronics, magnetic material, catalysts . . . so, I would say the life science is very important you see progress is made you hope also that it will pay off in the medical research.

I noticed that there are hospitals who are using more and more mass spectrometry to get information which is helping fight diseases. But I think with regard to materials then there you see that chemistry has changed over all the years, that they can handle these interesting systems, and they get used, and new materials, well we fly planes nowadays but the material from which they are made is quite different from many years ago.

GRAYSON: Oh [yes].

NIBBERING: Lower weight, lower fuel use, et cetera. I am not saying we should focus on one interaction. We should focus on more different directions. That is also the nice thing about mass spectrometry because it is applicable in so many fields. It is really multi-disciplinary.

GRAYSON: This probably leads into—or even as you maybe responded to this last question. What do you see the future of mass spectrometry?

NIBBERING: The future of mass spectrometry, I see that more and more miniaturization is occurring, simpler instruments . . . what is simple but at least if I may mention that the beginning of this week I was in the lab of Graham Cooks from the Purdue University who I know very well. They have developed of course their DESI but also Paper Spray and it is a very simple set-up and they use a lot of chemistry to get ionization that they apply that you get very good results and if you see the detection part of it, it is becoming miniaturized. I see that was also the messages which Graham transferred to me and I agree with that there is in the future [. . .] the fact that you will see more and more simple mass spectrometry based techniques which everyone can operate in organic chemistry labs, in clinical chemistry, in hospitals. I mean it will be a very normal method accepted by many disciplines.

GRAYSON: So it's just going to keep getting applied more and more, and more different areas?

NIBBERING: [Yes].

GRAYSON: Very good, well I think that gets it.

NIBBERING: It's okay?

GRAYSON: Oh [yes], looks good.

NIBBERING: Okay.

GRAYSON: Let's turn this guy off here and I push the right button.

NIBBERING: [laughter]

GRAYSON: Stop it.

NIBBERING: Delete it. [laughter]

GRAYSON: Yes . . . no, no, no, no.

[END OF AUDIO, FILE 2.3]

[END OF INTERVIEW]

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