# Aharon Loewenstein

Born Germany, 1929



**Ph-D thesis**: Hebrew University Jerusalem, 1958

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### Sabbatical leaves:

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### Major departmental responsibilities:

Chairman, Faculty Committee of Graduate and Undergraduate Teaching. Head, Physical Chemistry Section

# Major Technion's responsibilities:

Technion Graduate and Undergraduate Teaching Committee.

### **Field of Research**

Application of Nuclear and Electron Magnetic Resonance spectroscopy to kinetics and structure of simple molecules in the liquid state Studies of liquid crystalline phases Studies of chirality

## **Aharon Loewenstein**

לוינשטיין אהרן

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#### Scientific Autobiography and a little more.

התנצלות. ראוי היה לכתוב רשימה זו בעברית. התירוצים לכתיבה באנגלית הם: העדר מונחים עבריים להרבה מושגים מדעיים וחוסר הכישרון שלי להדפסה בעברית. על אלו, התנצלותי.

Background: I was born (31.01.1929) in Verden an der Aller, a small town some 20km south-east from Bremen, Germany. My father, Gustav, (08.08.1899-15.05.1971) was a lawyer. On April 7, 1933, he was dismissed from his profession by the Law of the Restoration of the Professional Civil Service that prohibited lawyers of non Aryan origin to appear in German courts. In June 1934, together with my mother, Hilde, (02.08.1905-16.9.1960) and my sister, Hanna (15.08.1932-) we immigrated to Palestine on board the ship "Polonia", departing from Trieste. My father obtained a 'Capitalist Certificate' (possessing more than 1000 Pounds Sterling) from the British mandate authorities. A few days after our arrival in the port of Jaffa, we traveled by bus (via Petach-Tikva, Qualqilia. Tul-Karem) to Netania. My father, together with my aunt (mother's sister, Herta) and her husband, bought the only existing small hotel in town from an American, Mr. Notkin. The hotel was built in 1933, had 6 guest rooms and was named Gal-Yam by Itamar ben Avi before my father bought it. I attended the local "Bialik" Elementary School from 1934 to 1942.

Much of what I tell below relates to my remote past and may not reflect precisely the true course of events. I trusted my memory and did not check documentation (wherever it exists) except for my list of publications.

My interest in Chemistry began at the Secondary Agricultural High School in Pardess Hanna (1942-47). I was sent to this school because education in Netania terminated with the 8<sup>th</sup> grade of the elementary school. The school was a boarding school, for boys only, though we had several girls in our class (who lived in the neighboring villages). The school had a five year program because in addition to the 'regular' High

224

School curriculum we studied Agriculture and worked on the school's farm. Thus I 'lost' one extra year at High School. I never felt sorry about the 'lost year' because the school, the teachers and my experience there were very pleasing. Our Chemistry teacher was Dr. Ashkenazi (nicknamed "Shleikes"). He was a pedantic teacher but performed his job very well. His teaching attracted and stimulated us. Together with a classmate and a good friend, Elkana (Kuni) Halevi, we assembled a 'Chemistry suitcase' that was an old suitcase filled with instruments and chemicals which were, legally or illegally, assembled from various sources, including the school Chemistry laboratory. We used to take our 'laboratory' to the center of our small orange grove and perform various chemical experiments. Fortunately, no catastrophe has happened. During my last (5<sup>th</sup>) year at school, Dr. Ashkenazi guit his position and was replaced by the elderly Dr. Rosenberg. Dr. Rosenberg has retired from the Kaddouri Agricultural School and his teaching of Chemistry was centered mostly on "Soil Science", namely the Chemistry and Physics of soils, fertilizers, colloids, etc. He was a dull teacher, reading his lessons while seated. Still, he was a kind person and presented us with the first introduction to topics that attracted me later. Some years later, while I lived in Rehovot working for my Ph.D., I was looking for jobs to supplement my poor income. Dr. Ashkenazi was the Head Master of a local High School (now the Amos Shalit School) and offered me a job to teach a one term course on the History of Science. My course was taken from a booklet containing lectures, written by several authors, in a series on the History of Science presented by the BBC. As far as I recall, my pupils seemed to enjoy my course. Till today I feel shocked by my boldness in accepting this job.

After graduation from my school (matriculation) I spent about two months in Beit Eshel (a very small settlement that existed about three km east from the old Beer Sheva). The reasons why I went to Beit Eshel were: a. I wished to spend a year of "National Service" by guarding the water pipe in the Negev. b. I was interested in soil mapping around that area and c. I had a cousin in Beit Eshel, *Aharon Heidemann*, whom I liked much. My plan could not materialize because I was not (yet) a member of the Palmach. In August 1947 I joined friends in the Tzofim Daled Hachshara and served in the Third Gdud (battalion) of the Palmach till my release in February 1949. The Third Gdud moved along the country during the war of independence (1947-49). Its main stations were: Beit Hashita, Ein Gev, Hulata, Ein Zeitim, Har Knaan,

Sarafend, Ramle, Shaar Hagai, Wadi Dorot, Beit Shean. In the summer of 1948 (July?), I attended a course for military reconnaissance (קורס סיירים) at Juara and that determined my job till the end of the war. I guided groups of people, from Negba to our northern positions in the Negev, through the Egyptian lines.

After the war of independence I became a founding member of Kibbutz Palmachim (April 1949). My knowledge and experience, in some agricultural professions helped me greatly. My main contribution to Palmachim was the establishment of the vegetable garden. A year or so later, I was strongly tempted to quit the Kibbutz and start studies at the Hebrew University. I could not decide as to which Faculty to register. The 'spirit of the time' (through the education at High School and the Palmach) suggested that I should study Agriculture (Agronomy) that was considered as the most useful profession to serve the State and the Kibbutz. On the other hand, Chemistry was my 'old love', so I searched for a reasonable compromise between the two. I was familiar (from my frequent visits to Beit Eshel during the mid 40's, with two young students who worked with Professor Rabikowitz (of the Faculty of Agriculture at the Hebrew University, located in Rehovot), on the project of soil mapping of Israel (at the time, Palestine). This project fascinated and interested me very much. I believe that I consulted them and eventually registered to a course on Soil Chemistry given by Dr Hagin at the Faculty of Agriculture of the Hebrew University (Professor Hagin is presently an Emeritus Professor at the Technion). The Kibbutz was quite antagonistic to this activity and in general to my academic aspirations (quote: "the time will come when we shall send our members to studies which we believe are needed for the Kibbutz"). Nevertheless, I traveled once or twice a week from Palmachim to Rehovot to attend the lectures and the laboratory exercises of Hagin's course. The course strongly convinced me that I should choose Chemistry if I wished to master properly Soil Chemistry (or Physics). The approach to this topic from the Agronomy point of view seemed superficial to me. Today, I doubt whether I had the capacity to make such a judgment and that the wish to learn 'pure' (as opposed to 'applied') Science was most likely the true (subconscious) motive. In the summer of 1950 I quit the Kibbutz and passed concurs examinations (in Mathematics and Chemistry) for the admission to Chemistry studies at the Hebrew University.

The teaching of Chemistry, especially Physical and Biochemistry, at the Hebrew University in those times was rather poor (an understatement). Considerable emphasis was put on practical Inorganic analysis and simple Organic synthesis and much of our time was wasted on these topics. Elderly teachers, who were dominant, followed the German traditions of the 30th. Quantum Mechanics was hardly mentioned and those who wished to learn it properly attended lectures by *Racah* given in the Physics Department. The mathematical background (needed for Racah's lectures and for other topics) was essentially nonexistent. To overcome these difficulties, those in my class who wished to specialize in Physical Chemistry, got hold of as many books as they could (this was neither simple nor cheap) and assembled in small groups for selfstudy. Thus, to a large degree, we were auto-didactics (which is not ideal). Some of the younger teachers in the Department were much better and outstanding among them were the brothers Aharon and Ephraim Katchalsky (later Katzir). A few years later, when I spent my postdoctoral years at Caltech and Columbia, I was quite shocked by my poor education in Physical Chemistry as compared to the young American graduate and undergraduate students.

The curriculum in Chemistry in those days led directly to the M.Sc. title (without the B.Sc.), after about five years of study. The fascinating lectures of Aharon Katchalsky on monolayers (in a Physical Chemistry course) convinced me to approach him and ask him to supervise my Master's thesis on that topic (another option that I considered, was the study of nitro derivatives of sugars with Yeshayahu Leibovitz). In his lectures Aharon played with the idea of a physical world reduced to two dimensions. His lectured were flavored with many historical anecdotes e.g. Benjamin Franklin 'experiments' with oil patches to calm the rough ocean waves, Miss Pockels novel technique for "cleaning" surfaces. etc. Aharon, at that time, was mostly interested in the physical chemistry of polyelectrolytes and consequently suggested to me to measure, using the Langmuir Balance, the interaction between a poly-acid (poly acrylic acid?) monolayers and ions dissolved in the water tray. Aharon had no experience with the use of the Langmuir Balance and asked Ora Kedem (who was also inexperienced in this technique) to assist me with the experimental work. Ora did her best to help me and I learned to appreciate her scientific and personal qualities. Poly acrylic acid is somewhat soluble in water and therefore quite difficult to spread on water-air interfaces. Consequently, we were

unable obtain reproducible results and most of that academic year (53-54) was spent in futile struggles with the instrument and the reading of most of the relevant published literature (that was still possible in those days). During the summer of 1954 I traveled abroad on a student exchange program to work in the Shell's Research Laboratories (BPM) in Amsterdam. I worked there for six weeks, on the qualitative and quantitative chemical analysis of hydrocarbon mixtures. This was my first true scientific experience. I worked in a real research (application) laboratory and towards the end of my stay was obliged to write my first detailed research report. With Aharon's blessing and recommendations I traveled to visit some research groups working on monolayer films in Utrecht and Cambridge (England). I learned much from these visits, in particular about the experimental aspects of operating the Langmuir Balance. After my return home, I joined the group of Israel Miller at the Weizmann Institute. He has just returned from a Sabbatical leave in the US and was experienced with monolayer work and the Langmuir Balance. He suggested new measurements using poly methyl methacrylate. Though the idea of measuring the electrostatic interactions between a poly-acid and counter-ions was abandoned, I produced some results, which enabled me to complete my Master's Thesis with some dignity.

Aharon agreed to accept me as his Ph.D. student but lacked the funds needed to support me (I believe that it was 200 I.L. per month). Shlomo Alexander, with whom I was acquainted during our study period in Jerusalem (he studied Physics), approached me and suggested that I should join him and Saul Meiboom to work on a new instrument, Nuclear Induction, which they were about to complete building (7kGauss or 0.7T, permanent magnet, ~ 31MHz for protons). Nuclear Induction was the term used at that time for what is now known as nuclear magnetic resonance (NMR). The name Nuclear Induction comes from the title of an article by Felix Bloch and from the fact that changes in the precession of nuclei spins induce currents that produce the resonances (a simplified version). Saul and Shlomo expected a visitor chemist from the US, Ernst Grunwald, (from Tallahassee Florida), who planned to do some chemical experiments with the new 'toy'. At that time Ernie was interested in acidity functions in non-aqueous media and hoped to measure the pKa values for alcohols in strong acid mixtures through NMR chemical shift titration curves. Unfortunately Ernie was unable to prepare the solutions (though he was a first class

experimentalist) because he was temporarily handicapped by a badly broken leg (the accident happened while crossing a street in London on his way to Israel, "Look Right, Look Left"!). Shlomo and Saul were incapable of mixing ethanol with sulfuric acid (too much to ask from physicists!) and thus Shlomo suggested that my duty in the laboratory (half of the time) would be devoted to preparing these solutions. For the other half of my time I should find some chemical problem, suitable for application with the new instrument and earn my Ph.D.. It was a risky decision to take. I did not have the slightest idea what Nuclear Induction was about and what could be done with it. Still, I gave my consent without too much hesitation because I was very impressed by Shlomo and Saul personalities and trusted their intuition and judgment. I started to prepare mixtures of ethanol and sulfuric acid but the measurements did not produce the expected S titration curves. Saul and Shlomo challenged Ernie to prove that chemists know what they were talking about. Ernie had to choose a system where he knew precisely what to expect: an aqueous solution of methyl ammonium chloride. The pKa value for this molecule is well known so that the titration curve (the methyl resonance chemical shift as a function of the pH), must produce the desired S shape curve. This choice determined the fate of my Ph.D. thesis and most of the future of the Nuclear Induction laboratory at the Weizmann Institute.

When we performed our first measurements in aqueous solutions of methyl ammonium chloride, we were quite surprised by the different spectra in acidic and basic solutions. Once we understood what these differences meant and consequently that one could obtain quantitative reaction rates from the different spectral lineshapes, the study of fast chemical kinetics (proton exchange), became the prominent activity topic of our laboratory. Obviously, the 'problem' of a search for a topic for my Ph.D. thesis, was now completely solved. There existed a very large number of interesting chemical systems where the measurements of these kinetic parameters was (and probably still is) important. Our only 'problem' left was where to start! Till today, nuclear magnetic resonance is one of a few techniques for the measurement of very fast (and also very slow) chemical kinetic processes. The unique features of this technique are the application of an "internal clock" (i.e. the inverse chemical shift, spin-spin or dipolar interactions) for the evaluations of the kinetic parameters and the possibility to measure rates at chemical equilibrium, that is with K=1 (e.g.,  $H_2O+H_2O=H_2O+H_2O$ ).

I worked very intensively with *Saul* and *Ernie* (often from noon to next morning,) on the measurements of proton exchange in ammonium salts. Also, in cooperation with *Arie Berger* we measured proton exchange reactions in a simple amide and with *Michael Anbar* we followed proton exchange kinetics in hydrogen peroxide-water mixtures. It was a period where we obtained truly new results in each working session. The more we progressed with our work, the more we realized the enormous potentialities of the technique. This experience hardly reoccurred in years to come. To pay an old 'debt of honor', we eventually also measured the "S" titration curve for methyl ammonium chloride. I might add that during that period I also synthesized a compound ( 2-methyl 2-nitro, 1.3 propane diol) that *Shlomo* needed for his studies on the non equivalence of certain methylene protons.

During that period I experienced for the first time the potential usefulness of a computer in scientific research. The modified Bloch equations (by Harden McConnell) for the spectral lineshapes, had to be solved for different values of exchange rates, relaxation times etc. This we did manually on electro-mechanical calculating machines before the home built electronic computer, "WEIZAC", became operative. *Pinchas Rabinovich* (a mathematician from the Applied Mathematics Department) assisted us in the programming (machine language). This was (I believe), the first use of a computer for basic research purpose, in Israel. I spent many nights near the huge machine (a room filled with electronic glass tubes that produced much heat) watching and controlling the array of blinking small lights (binary zero-one indicators). I rechecked some of the results manually because I distrusted the machine. *Saul* succeeded in obtaining a grant (after some political difficulties!) from the US navy. With this money we issued a booklet with some of our numerical calculations for the lineshapes of collapsing exchange doublets, triplets and quartets. It became a 'best seller' in NMR laboratories around the world.

After two years (1958) I had more than enough material for a fairly respectable Ph.D. and planned to go to the US for a post-doc position. Two anecdotes related to my Ph.D. thesis: a. While writing it I wished, naturally, to consult *Saul Meiboom* on the text. Since *Saul* was not fluent in Hebrew (my thesis was written in Hebrew), he suggested that I should come to his home one evening and read it to him. *Saul* was

lying on his sofa listening to my reading but within a few minutes was deep asleep. That was the first and last time he 'read' my thesis. b. Another referee, *Gabor Stein* from the Hebrew University, asked me to come and 'discuss' my thesis with him (a very common procedure). When I entered his office he greeted me with: "What an interesting thesis!" then started to look for it on his desk. I pointed out to him the brown envelope hidden in a pile of papers and he pulled it out. It was unopened! My referees for the Thesis were *Israel Dostrowsky, Willy (Zeev) Low* and *Gabor Stein*. Other newcomers to the laboratory, *Zeev Luz, Mati Sheinblatt, David Gill* and *Avraham Szoke*, made further impressive progress with studies of proton exchange in various systems containing N-H and O-H bonds and also important modifications of the experimental techniques such as the well known CPMG pulse sequence. All were much assisted by the very skillful contributions of our electronic technician, *Moshe Sasson*.

My first post-doc position (1958-59) was spent at the California Institute of Technology (Caltech) with Jack (John D) Roberts. I was awarded the Fulbright Travel Fellowship that was very important financially under the circumstances at that time. The fellowship provided me and my wife Rachel with return air tickets to the US (unlimited stopovers) + shipment (by air) of 70 kg personal luggage + health insurance in the US. Rachel and I fully exploited the benefits of this fellowship for an extensive tour through Europe that lasted for about three months. My first meeting with Jack was, on my way to the US, at the Kekule Conference in London. I had hoped to learn from him some Organic Chemistry applications of NMR (he later wrote two small books on NMR applications in Organic Chemistry). Jack however wanted me to do what I was best trained for, namely chemical kinetics. He proposed to study the (nitrogen) inversion process kinetics in methyl aziridine. The study of this system has been attempted earlier, unsuccessfully, in his laboratory and I contributed to its completion. My 'counter' suggestion was to study the ionization pattern of a tricarboxylic acid (e.g. citric acid), by NMR. This project, which I actually started at Caltech was finalized some years later, together with one of my first graduate students. Haggai Gilboa. The year at Caltech was very enjoyable both scientifically and socially. The weekly physical chemistry seminars were excellent and the course on magnetic resonance given by Harden McConnell broadened my scientific education significantly. In Pasadena I met future friends, Cafiero Franconi (Physics),

*Gideon Fraenkel* (Chemistry) with whom I enjoyed scientific cooperation in years to come.

My second post-doc year was spent at Columbia University in New York with Ben Dailey. The main motive of going there was my fascination from the big city that I visited briefly on my way to California. I had hoped that at Columbia I should take an interlude from NMR and learn a completely new (for me) technique: microwave spectroscopy. The circumstances were, however, unfavorable for such an enterprise because it so happened that Ben was not scientifically active during that particular academic year (1959-60). The option to learn microwave spectroscopy from two of his Post-Docs (Turner and Westerkampf) turned out to be impractical since they struggled with too many experimental and theoretical difficulties. Had I known before that such would be the situation at Columbia, I would probably have stayed at Caltech. I 'consoled' myself by returning to the exchange problems in ammonium salts and otherwise enjoyed the immense cultural resources of New York. Together with Tom Connor (a post doctoral fellow from Oxford), we measured the activation energies of proton exchange in all simple ammonium salts (methyl to trimethyl). The rather unexpected results which we obtained were the cause of an intense scientific dispute with Ernie who worked at that time with Saul at Bell Labs (Saul had left the Weizmann Institute and accepted a position at Bell Labs) and also served as a referee of the paper that Tom and I submitted to the JACS. Ernie believed that some of our results made no sense but could not refute the experimental data and could not produce convincing arguments to support this view. I shared some of Ernie's skepticism and challenged him to repeat our experiments. To my best knowledge, these measurements have not been repeated since, except for the trimethylammonium chloride case which was done by Ernie and agreed with our measurements.

I returned to the Weizmann Institute in the summer of 1960, several months earlier than planned because of my mother's terminal illness. The "Nuclear Induction" Laboratory was still mostly busy with work related to proton exchange and was temporarily headed by *Shlomo*. I took his position when he departed for his Post-Doc position (at UBC) and waited for *Saul* to return. I hesitated to start some new projects of my own and consequently continued along the line of my Thesis. With *Avraham Szoke* I measured the activation energy for proton transfer in water and with *Moshe Sasson* I developed a novel (primitive but working) spin echo attachment to the Varian DP60 spectrometer. *Tom Connor* visited me in May 1961 and we wrote a review on proton exchange measurements by NMR. With another guest *Windelt Drenth* (an Organic Chemist from Utrecht, Holland), we studied the NMR spectra of several ethers and thio-ethers.

I accepted an offer from Otto Schnepp and David Ginsburg to join the Chemistry Department at the Technion and moved there in September 1962. The Chemistry Department at that time was located in the Hadar campus of the Technion. The move meant that from now on I am the master of my activities and for the first time I could decide on my research program. I established my laboratory with adequate equipment (a Varian DP60 spectrometer with several attachments). The Chemistry Department, including my laboratory, moved to the new campus in 1964. My basic interest was still focused on the measurements of chemical kinetic processes by NMR. However, I wished to broaden its scope to electron transfer reactions and to a more basic understanding of the mechanisms, especially the role of the solvent in the kinetic processes. Another aspect of NMR which caught my imagination was the study of the "less accessible" (as they were called at that time) nuclei such <sup>14</sup>N, <sup>59</sup>Co, <sup>95</sup>Mo, <sup>53</sup>Cr, <sup>131</sup>Xe and others. The Varian DP60 spectrometer was equipped for these studies though it suffered from all the limitations of the pre-FT NMR period. These topics, chosen partly as "fun" and partly as curiosity to explore novel territories, brought me into the realm of inorganic chemistry. My first graduate students at the Technion were Mordechai Shporer and Haggai Gilboa. With Shporer and in cooperation with Gill Navon (and later also with Gideon Ron) we investigated rather extensively several cyano-metal complexes in aqueous solutions including studies of electron transfer between ferri- and ferro- hexacyanide ions. Together with another student, Yair Egozi. I investigated the electron transfer in the chromate-dichromate system through the <sup>53</sup>Cr NMR measurements. Our studies of <sup>59</sup>Co resulted in an unexpected bonus: due to the very large chemical shifts of <sup>59</sup>Co, we observed some interesting isotope effects. By chance I learned that Paul Lauterbur was also interested in isotope shifts, which resulted in a joint publication with him. With Haggai Gilboa I returned to the study of the ionization pattern of citric acid that I begun in Pasadena with J.D.Roberts. This time however, the issue was treated properly and also extended to several other tricarboxylic acids and their derivatives.

Further on, in cooperation with *Haggai, Janina Altman* and *David Ginsburg*, we studied the kinetics of ring inversion in cis-decalins and in a propellane.

I spent two months in the summer of 1963 at the Varian facilities in Zurich by the invitation of its director, Warren Proctor. I tried to convince Varian Associates to develop commercially a spin echo attachment for the DP60 which Moshe Sasson and I have built. Unfortunately, I did not foresee FT NMR and my sole aim was a pulsed spectrometer for relaxation times and translational diffusion measurements. Warren's reaction to my initiative was very favorable. However, Varian headquarters in Palo-Alto ruled against the project on the basis that the market for pulsed spectrometers is rather limited (the argument was that most NMR users are organic chemists who are not interested in pulsed spectrometers). Bruker's success in introducing the first pulsed spectrometer (and consequently its technical readiness for the FT epoch) proved that Varian's decision was a big mistake. During that visit to Varian I became acquainted with Paul Rigny. Paul was sent to Varian by his Thesis supervisor, Lionel Solomon, to become acquainted with practical NMR. Together with *Paul Rigny*, Atillio Melera and W.Walter (an organic chemist from Hamburg who supplied he materials) we measured the activation energies for rotation barrier around the C-N bond in several thioamides and compared them with similar results for amides. This topic was studied later in great detail, both experimentally and theoretically, by many researchers.

Around 1965-6 I decided that magnetic resonance activities in our Department should be complemented by Electron Spin Resonance (esr) studies and I purchased a Varian esr spectrometer for this purpose. I persuaded my Ph.D. student, *Rafi Poupko*, to work with me on the new spectrometer. Our first project was the study of the kinetics of proton exchange in radicals derived from simple aliphatic alcohols and compare the results to those obtained in their parent alcohols (*Luz*). For the production of the radicals, we used a Ti<sup>+3</sup> salt and hydrogen peroxide in a flow system. Furthermore we derived a large variety of radicals from amino acids, more complex alcohols and other materials. This opened the way to analyze systematically the hyperfine couplings (spin density) in small organic radicals. In 1967 I convinced *Brian Silver* who then worked at University College, London (I knew *Brian* earlier from his stay with *Luz* at the WIS) to join our staff. *Brian* took over most of the esr

research and became a co-supervisor in *Rafi*'s Ph.D. Thesis. It seems that in those years my research directions were rather divergent and covered broad fields. I liked it this way (and still do).

My first Sabbatical (67-68) was spent in Oxford with *Rex Richards*. I was a Visiting Fellow at All Souls College and received scholarships both from the College and the Royal Society. In order to permit me to dine at High Table without paying, I was awarded a M.A. degree from the University of Oxford (cost: 10 Pounds, paid by All Souls). During the year I was well trained in all the bizarre manners of Oxford dons. My time during that year was occupied mostly by the work of my students at the Technion. I persuaded *Peter Atkins* (Lincoln College) to work with me on the problem of the theoretical interpretation of the magnetic relaxation data in liquid ammonia (protonated, deuterated and mixed species) that *Yair Margalit* had measured. This cooperation resulted in a rather complicated model (most probably wrong) for molecular dynamics in liquid ammonia.

Around that period (about 1967), my interest shifted from the kinetics of chemical reactions to molecular dynamics in liquids. I had the impression that the gaseous and solid phases were, at least in principle, pretty well understood. The complexity of molecular motions in the liquid state intrigued me to explore how much related information could be obtained from measurements, by NMR, of the  $T_1$  and  $T_2$ relaxation times and the translational diffusion coefficients. My measurements of relaxation times were mostly confined to quadrupolar nuclei because their interpretation is fairly straightforward while the interpretation of the relaxation data of dipolar nuclei are considerably more complex. With time I acquired a fairly broad view on this topic and realized the inherent limitations and advantages of the application of various NMR techniques. I started with very little knowledge (an understatement!) of the physics of the liquid state. An obvious solution to my problem was to organize a School (Workshop) on the physics of the liquid state and learn from it as much as possible. This I did during two weeks in September 1971 with the financial help from the Bat-Sheva foundation. I invited top experts in the field of physics of the liquid state (Oppenheim, Litowitz, Kivelson, deGennes, Zwanzig, Bratos, Freed, Ben-Reuven, Bixon, and others). Most experimental techniques and related theoretical topics for the study of liquids were presented in the School. I

believe that the School was a success. Particularly through the lectures of *deGennes*, I became familiar with liquid crystals and appreciated their importance for the measurements of the anisotropy of molecular reorientations in the liquid phase. I also realized that measurements of solutes in liquid crystalline media extend considerably the possibilities offered by NMR spectroscopy since in isotropic media dipolar and quadrupolar interactions are 'washed out' (residual values of dipolar interactions in weakly ordered media are nowadays termed RDC).

As mentioned above, my first enterprise in the study of dynamics in the liquid state was with *Yair Margalit*, in cooperation with *Peter Atkins*, through the measurements of <sup>14</sup>N and deuterium relaxation times in liquid ammonia. Later, with *Yair Egozy*, in cooperation with *Brian Silver*, we studied the deuterium relaxation of deuterated benzene dissolved in a nematic liquid crystal. The main purpose of this study was to obtain information on the anisotropy of benzene reorientation in a liquid crystal. This, admittedly, was a rather bold project for its time. Some years later this topic was studied extensively with much improved experimental and theoretical tools by others. These projects signaled a new (slightly more focused) direction in my scientific activity that lasted for about 20 years.

In the course of scientific research it might happen that a sidetrack turns into a new main avenue. This, happened to me when I read a paper by *Saul Meiboom* who discovered that tetramethylsilane is apparently distorted, from its nearly spherical shape, when dissolved in a nematic liquid crystalline media. I was somewhat skeptic about the result but my skepticism antagonized my faith in *Saul's* scientific qualities. Thus, I decided to try it myself. I started with neopentane, then with methane and finally with xenon atoms (!). In all cases the apparent distortion was observed beyond doubt (*Saul* was right again, as always.). I soon realized that, this phenomenon is closely related to that which is observed for symmetric cations and anions (such as sodium, lithium, ammonium etc.) belonging to soap molecules of lyotropic liquid crystals (though there exist some significant differences). I worked on these topics with several coworkers: *Roman Ader* (methanes, silanes and cobalt complexes), *Manuel Brenman* and *Rachel Schwartzman* (Xenon, various cations in lyotropic systems), *Jean Charvolin* and *Joseph Virlet* (cations). A set of experiments on this topic, which unfortunately were never completed, was performed with *Jean Pierre* 

Kinzinger in Strasburg, (measurements performed at the Bruker laboratories near Karlsruhe and in Wissenbourg). The idea was to dissolve cations a non-aqueous media (to eliminate the possibility of non-spherical distribution of water dipoles around the cations (i.e. non-spherical hydration) and then 'distort' them in a non aqueous liquid crystal. The systems chosen were alkali halide salts complexed with cryptates (2,2,2, ; 2,2,1, 211) and dissolved in PBLG/organic solvent liquid crystals. We obtained quadruplar splitting (triplets,) for sodium but none for several other alkali cations. This work still awaits its completion. With time, some progress, theoretical and experimental, has been achieved on the general problem by other groups, mostly by Diehl and, Jokkissari in Basel and Oulu (Finland), Burnell and deLange in Amsterdam and Vancouver and by Lindmann, Wennerstrom and others in Lund. Till these days I am convinced that we do not yet possess an adequate theoretical model needed to interpret many experimental results. The phenomenon is quite unique because, as David Buckingham has correctly pointed out to me rather early in the game, NMR is capable of detecting very tiny molecular, atomic or orbital 'distortions' from their shape in a dilute gas phase. These 'distortions' result from the anisotropy of the intermolecular potentials prevailing in ordered media and seem to be rather difficult to calculate. Thus, I believe that the case of the 'apparently oriented spherically symmetric species' still awaits its proper solution.

In the autumn of 73 a Post-Doctoral fellow from the US, *Mike Piliavin*, came to work with me. He was a theoretical Chemist (Physicist?) and proposed to work on the simulation of phase transitions in nematic liquid crystals by the Monte-Carlo technique (this followed a published work by *Lasher*). His suggestion was good but involved enormous programming work. Rather slow computer facilities were available at the Technion and some attempts were performed at the computer of the Weizmann Institute. Year 1973 was quite bad for scientific research because of the war and its after effects. *Mike* ended his stay with me without, unfortunately, getting any meaningful results.

My second Sabbatical (74-75) was spent again in Oxford. I decided to devote it to time resolved esr, in cooperation with *Keith MacLauchlan*. *Keith* developed this technique and had the only laboratories in the world who was equipped to perform such experiments. My idea was to measure the esr spectra of the photo-dissociation

products from duroquinone dissolved in a nematic liquid crystal. We assumed that due to the anisotropic diffusion of the product radicals in the liquid crystalline media, their spectra would enable us to discriminate between the, so called, "radical pair" and "triplet" mechanisms in the process of photo-dissociation. The issue of "radical pair" vs. "triplet" mechanisms in photo-decompositions was rather controversial and no experimental technique was available to distinguish unambiguously between them. In this project I cooperated with Luigi Pasimeni from Padova who spent the year with Keith. We worked very hard with no meaningful results. This caused a very great disappointment to both of us. The reasons for our failure were eventually well understood: At that time, no aliphatic nematic liquid crystals were commercially available and we were obliged to use 'conventional' materials (like EBBA) that contain benzene rings. In such materials most of the light (from the N<sub>2</sub> laser) was absorbed by the solvent. Furthermore, the light intensity was insufficient and the yield of the product radicals was very low. On top of all, Keith's instrument was an elaborate first model and rather difficult to operate. Despaired by the lack of progress, I turned to a project of measuring the magnetic relaxation times of a probe (nitrobenzene) dissolved in a liquid crystal, close to the nematic-isotropic phase transition point. The aim was to detect changes in molecular dynamics in the pretransitional range. This work was performed in cooperation with David Turner who belonged to Ray Freeman's group.

Another interesting sidetrack was the measurements and exploration of quadruple coupling constants (QCC) of deuterium, nitrogen and other quadrupolar nuclei, in small molecules. These so called 'constants' are very sensitive to changes in the environment of the nuclei in the molecules (e.g. hydrogen bonds and specific intermolecular interactions). There exist accurate methods to measure the QCC's in the gas and the solid phases but difficulties arise in the liquid state. In the liquid state, QCC's must be derived from an expression which contains two unknown parameters (one of them being the QCC). NMR can be applied but with some severe limitations that we studied in detail. I have studied several systems: N<sub>2</sub>O and NH<sub>3</sub> (with *Manuel Brenman*), the azide (N<sub>3</sub><sup>-</sup> ion), ammonium nitrate (with *Haggai Gilboa*) and dimethylsulfone (with *Dan Igner*). The latter study was a rather unique study that involved the NMR measurements of <sup>33</sup>S and <sup>17</sup>O nuclei (in very low concentrations) and computational work concerned with finding the direction of the main component

of the electric field gradient tensor of the sulfur atom (performed by *Miri Karni*). I also set out to measure hydrogen (and HD, D<sub>2</sub>) dissolved in a nematic liquid crystal. This is a tricky experiment because of the difficulty in preparing the samples. We were just about ready to start these measurements when an exellent paper by *Burnell* and *deLange* appeared (in JPC), in which they presented a detailed and complete experimental and theoretical work on precisely this problem. I decided to quit. In 1983 I wrote a review (invited by *J.A.S. Smith*) on the subject of the measurements and interpretation of quadrupole coupling constants by NMR. In this review I described in detail the complexity of the problems and the difficulties to solve them.

An interesting, though futile, attempt was attempted in 79-80 together with *David Goldsmith* (a post doctoral fellow from the US): The idea was to measure changes in the NMR relaxation times of liquids (and liquid crystals in particular) while an acoustic perturbation is applied. Rough theoretical estimates (begun by *Peter Atkins*) indicated that under certain circumstances we might measure variations in the  $T_1$  values when an acoustic perturbation (of the right frequency) is applied. The expected effect originates from non- linear density fluctuations in the liquid caused by the acoustic perturbation. Unfortunately we were inexperienced with acoustic techniques and unable to complete a successful experiment. We devoted great efforts to this project.

On the main track, apart from the work mentioned above, I extended the ammonia work to liquid methyamines (with *Ruth Waiman* and *Esther Glaser*) and to nitromethane (with *David Goldsmith*). I believe that the most interesting and exiting results were obtained in the measurements of the anisotropic translational diffusion coefficients of methane dissolved in thermotropic liquid crystals that possess nematic and several smectic phases. Methane is (almost) an ideal probe for such measurements because of its weak interaction with the solvent. This work was performed with *Mike Moseley* using facilities available at the Weizmann Institute. It produced results for the parallel and perpendicular diffusion coefficients in several liquid crystalline phases. These results present a challenge for theoreticians (*Pier-Luigi Nordio* has shown great interest). I regret that we were unable to extend this work.

An interlude: Sometime during 1980 or 1981, through the initiative of *Izhack Oref* and in cooperation with our colleague *Zvi Dori*, we started to discuss the idea of establishing a Science and Technology Museum in Haifa. A self appointed committee for this purpose has existed but did not succeed to materialize the idea. In February 1983 the first exhibition hall was opened on the site of the old Technion campus in Hadar. In the early stages of the Museum, initially named "Technoda", my main activity was the organization of weekly lectures for the general public on scientific themes. I served on executive board of the museum til about 1996.

I spent my third (1982-3) Sabbatical in Orsay (Universite Paris-Sud). It was originally planned to be in the Saclay (CEA, Atomic Energy Commissariat facilities) but could not be materialized due to political reasons (Israeli activities in Lebanon). *Jean Charvolin* has shown me some very preliminary results that he had obtained in a lyotropic liquid crystal composed of a dicarboxylic acid and solvent. The structure and phase behavior of lamellae (or other lyotropic structures) for molecules containing two polar ends attached to an aliphatic chain, intrigued our imagination (e.g., is the chain straight or folded into loops?). I started to work on the subject in Orsay and did most of it after I returned home. Much of the work was performed at the Weizmann Institute with *Helen Gutman* and in cooperation with *Zeev Luz, Rafi Poupko* and *Herbert Zimmermann*. We studied several bifunctional (dicarboxylic acids) lyotropic systems and studied their phase diagrams that included a reentrant isotropic phase (we expected a cubic phase!). We have also studied the perturbations induced by the addition of short-chained mono- and di- acids to the these systems.

During that Sabbatical I have persuaded *Charles deMenorval* who worked in the laboratory of *Jacques Fraissard* at Universite-Paris 6, to cooperate with me on NMR measurements of <sup>129</sup>Xe and <sup>131</sup>Xe binding to water (clathrates) and proteins in aqueous solutions. We measured the chemical shifts for <sup>129</sup>Xe and the line-widths for <sup>131</sup>Xe in the same samples. Preliminary measurements were very promising but unfortunately time ran short and I had to return home before we could complete this study. <sup>129</sup>Xe NMR has recently found many applications, due in particular, to the use of hyperpolarized Xe which enhances tremendously its NMR sensitivity.

My interest in carbohydrate liquid crystals originated in a Colloquium given in our department by the crystallographer, *George Jeffrey* from Pittsburgh. He presented X-rays results for sugar based carbohydrates (non-ionic soaps) that form various liquid crystalline phases. The interesting part, for me, was the fact that these materials form both thermo- and lyo-tropic liquid crystals. I imagined that manipulations of the systems (e.g. using the and anomers, changing the length of the length of the aliphatic chain attached to the sugar, changing the nature of the solvent or the temperature), would create a broad and interesting panorama of experimental possibilities. Indeed, as I began (in cooperation with *Dan Igner*) to obtain results with

-octyl-glucopyranoside in water, benzene and mixtures of benzene and/or water, these expectations were materialized. *Uri Zehavi* (of Faculty of Agriculture at the Hebrew University) kindly assisted with the deuteration of the octyl side chain and *Geoffrey Luckhurst* and *Andrew Emerson* cooperated in the calculations of the order parameter profile of the side chain. Further work on homologous series of the - octyl-glucopyranoside (all with *Dan Igner*) revealed the richness of the phase diagrams. Although several other carbohydrate liquid crystalline systems have been studied since, mostly by DSC, X-rays and optical microscopy, the fundamental understanding of the nature of the phase diagrams, "leaves much to be desired". Some of the peculiarities in these systems are truly amazing, for example, the differences noted for the and the anomers, the appearance of cubic phases and many other effects.

Sometime during 92 I received a copy of an obscure Journal, "Molecular Materials", in which one paper (by *Bykov* et al) caught my attention. It concerned a columnar ('chromonic') lyotropic liquid crystal based on aqueous solutions of a red dye, benzopurpurin. I had some previous experience with a well-behaved chromonic liquid crystal, DSCG / water and decided to have a closer look at benzopurpurin /  $D_2O$  mixtures by deuterium NMR. The work was performed with *Manuel Brenman*. It was not an easy task to assign the different phases of chromonic systems by NMR (we tried also X-rays measurements but had limited access to the instrument and too little experience). Our published work leaves many questions unanswered such as the fact that very low concentrations of the dye are producing ordered phases, the extreme sensitivity of the nature of the phases to the chemical structure of the dye, the structure of the phases, and others.

My latest (presumably last) scientific adventure which could be termed "chirality etc", started in a bizarre manner: I spent the 88-89 academic year on a sabbatical in Cambridge, England, hoping to do some solid state NMR with Jacek Klinowski that for one reason or another came to nothing. Most of that year was devoted to reading and to the cooperation with the Southampton group (Geoffrey Luckhurst, Andrew *Emerson*) on the interpretation of the side-chain dynamics of carbohydrate liquid crystals. Towards the end of the year I noticed a paper by Jacques Courtieu, from Orsay, on the measurements of <sup>129</sup>Xe chemical shifts in various liquid crystalline phases. I wrote to Jacques, complimenting him on his paper and suggested to discuss some further possibilities of work with him on Xe. In response I was invited to spend a month with Jacques in Orsay (summer 90). I accepted the invitation willingly. Upon my arrival Jacques presented the work currently performed in his laboratory which included the application of 'compensated' cholesteric liquid crystal mixtures with the purpose of measuring different NMR spectra for enantiomers. This project followed very similar experiments performed many years earlier by Saul Meiboom! The mixtures that Jacques used were sensitive to the temperature, composition and mode of sample preparation and did not seem to be suitable for the purpose of obtaining different NMR spectra of enantiomers. Furthermore, Meiboom's experiments could not be reproduced. This was rather amazing to me, recognizing the experimental capabilities of both Saul and Jacques. I suggested to use solutions of poly- - benzyl-L-glutamate (PBLG) instead of the 'compensated mixtures'. I had some earlier experience with PBLG solutions through my work with <sup>131</sup>Xe as solute and other studies. We tried it immediately and it worked perfectly! Being, both of us, very enthusiastic with this result, we forgot all about our planned Xe project and devoted the next 10 (and more) years to develop a novel and elegant technique for chiral discrimination by NMR by using chiral liquid crystalline solvents. In a sense, this project 'closed a cycle' for me because it started with the attempts of Jacques to elaborate on some early results of Saul Meiboom.

My collaborators and friends in Orsay were Jean Marie Pechine, Jean Pierre Bayle, Isabelle Canet, Abdelkrim Meddour, Philippe Lesot, Willy Smadja, Philippe Berdague, Denis Merlet and of course, Jacques Courtieu. Other members of the laboratory assisted in many ways over the years. I spent in Orsay two half Sabbaticals and many shorter visits.

Chirality is a fascinating subject. One aspect that is far from being properly understood, is its quantitative evaluation. I made some efforts to correlate our experimental results which are basically probing the intermolecular interactions (through their effect on the ordering), with some quantitative chirality measures (*Avnir*, *Osipov*, *Moreau*, *Gilat* and others). Another important challenge would be to understand the molecular details of the chiral discrimination that is, the interaction between the poly amino acid and the solute. This can be done by designing clever experiments and/or through theoretical computations. I tried to convince (and still am) experts in molecular dynamics to cooperate with me on this problem. I think that such computations, in light of our present results and through newly planned experiments, could shed light on the mechanism of chiral recognition in Biology. The system which we used (PBLG + organic solvent) is on one hand simple enough for physical modeling and on the other hand not too remote from real biological systems.

Hardware: Instrumentation is of tremendous importance in NMR since it determines what you can do and what you can not do. Occasionally I went to perform experiments in other institutions such as TAU, WIS and other places as I was unable to perform them at home. As told above, my first instrument was a home built (mostly by *Saul Meiboom, Shlomo Alexander* and later in part by *Moshe Sasson*) 31MHz (protons), corresponding to 0.7T permanent magnet. This instrument was a modified version of the Bloch - Arnold instrument that existed at Stanford. It was the only NMR instrument in the world that had a built in cigarette lighter, battery operated. *Saul, Shlomo* and I used this gadget quite a bit! My first instrument at the Technion was the Varian DP60 (60 MHz protons, 4T electromagnet). It was a state of the art instrument. Later arrived the Bruker HFX 90 and the BKR322S pulsed spectrometer, both operating with a 2.1T electromagnet, 90MHz protons. Finally I worked with the Bruker WH400 that operated with a 9.4T wide bore superconducting magnet (energized on 31.01.1985).

NMR instruments are technologically complicated gadgets and a talented service person is essential for their proper routine operation. When I started my work at the

Technion, I searched an electronic technician and eventually found *Aharon Peer* for this position. *Peer* served the NMR facilities (and other scientific instruments in the Faculty) for several decades with great talent and capability. He solved many difficult technical problems and thereby contributed significantly to many research programs.

My early dreams of investigating the Physics and Chemistry of soils failed to materialize. One of the reasons was that NMR techniques were not yet properly developed, during most of the period, to handle such problems. Towards the end of my career the situation changed. A few years before my formal retirement (1997) I made great efforts, in cooperation with researchers from the Chemical Engineering Faculty and others, to acquire a micro-imaging NMR spectrometer. Such an instrument would have enabled me to study the anisotropic diffusion and several other properties in heterogeneous systems, such as soils. Unfortunately, my efforts did not bear fruits and I was not able to acquire this instrument.

About two decades ago, I became interested in some particular 'non-scientific' themes. Initially my interest was directed to the fate of German Jewish scientists who were expelled from Germany by the Nazis in 1933. The expulsion of my father, who was a lawyer, may have triggered this interest. The first question that interested me was the reactions of the Aryan scientists to the dismissal and expulsion of Jewish scientists. I could not understand how most of the eminent, well educated, intelligent, scientists, did not react or protest in reaction to such malicious acts (that was still possible, to some extend, in early phases of the Nazi regime). The behavior of the German scientific community puzzled me. A possible answer to this question I received from the geneticist, *Benno Muller-Hill* from Koeln, who attributed the behavior of the Aryan scientists simply to their greed and aspirations to power. This answer, which sounds simplistic, may be the correct one (with a proper admixture of Anti-Semitism). During my meeting with him I also befriended his student *Ute Deichmann* who was, at that time, writing her Thesis on Biology and the Biologists in Germany during the Nazi regime. Ute has contributed significantly to historical studies of scientists in

Nazi Germany and in particular to those of Jewish origin who were compelled to emigrate.

With the years my interests broadened and included the relationship between Scientists and the State or, in other words, the inherent conflict between loyalty to one's moral principles and his obligation to his state homeland. This topic is not specific to totalitarian regimes as the Nazi Germany or the USSR, but relevant also to democratic regimes, such as the United States or England. The development and construction of "non-conventional" weapons (atomic, biological and chemical) by scientists for their homelands, is the case where the conflict between personal morals and national duties is manifested.

To what degree scientists should be politically or socially involved, is another aspect of the same issue. Personally, I was active in the "protest movements" that arose after the Yom Kipur war. Later, I tried two or three times to be politically involved. However, these naïve attempts ended after very short periods, with great disappointment from the way the political system is run.

My interest was centered mostly around the period of the second world war, when the issue of political attitudes of scientists, arose through the development (or attempts to, in the case of Germany) of atomic weapons. A much discussed and well documented case is that of Werner Heisenberg (the "white Jew"). Did he do the best he could to provide the regime with atomic weapons that would lead Germany to victory? Or did he play some clever games just to do the contrary? I believe in the first option. Other examples are the scientists who participated in the Manhattan project at Los Alamos. Almost none of them quit the Manhattan project that was constructed against Nazi Germany, after it became definitely known that the Germans were far behind with their programs or even after the total collapse of Germany in May 1945. A very few exceptions, such as Rotblatt and some others, quit their participation in the construction of the bomb. A few others (L.Szilard, J.Franck, E. Wigner) tried to prevent the bombing of Japanese cities.

One of the early books that described some of the background to these issues was "The making of the Atomic Bomb" by Richard Rhodes (1986). Since then I have read

some of the vast literature that is concerned with these topics. This eventually produced a small article ( published in "Jews and Sciences in German Contexts", U. Charpa and U. Deichmann Ed., Mohr Siebeck, 2007) on a somewhat related issue that occurred before WWII (1938).

Teaching: I worked 35 years at the Technion (1962-1997). During that period I spent 5 years on Sabbaticals (Oxford, twice; Cambridge; Paris, twice). It may be appropriate to conclude these notes with a short review of my teaching experience.

In the very early years I considered teaching as a nuisance and an unavoidable perturbation to my research activity. I did not think that it is worth a great effort, in particular to students who were not Chemistry majors. I was inexperienced in speaking to a large audience and on at least one occasion, lost my voice! The Laryngologist whom I consulted called it "the teacher's disease" and advised me to take a course in speech training. I believe that my teaching qualities at that time were rather awkward and that my performance was unfair to the students. With the years the situation has improved much though I never reached the status of a "distinguished teacher" and my marks in the student's Teachers Quality Questionnaire were mostly mediocre. Gradually I learned to appreciate the importance of good teaching and devoted more and more time to its fulfillment. I gave courses on most topics of Physical Chemistry (Thermodynamics, Kinetics, Surface Chemistry, Spectroscopy) to undergraduates and specialized courses on NMR to both graduate and undergraduates. In the early years I gave a course on NMR at what is now known as Ben-Gurion University in Beer Sheva and a course on Fast Chemical Kinetics at the Weizmann Institute of Science. I served for 9 years on the Technion Committee for Graduate and Undergraduate Studies and for about 3 years as Chairman of the Faculty Committee for Graduate and Undergraduate Studies. I admit that I now hold a very different opinion in the matter of teaching from that which I had in the beginning of my career. I enthusiastically participated in dissipating science to broader audiences such as to High School pupils, soldiers and adults. I gave (and still do) popular talks on topics such as MRI, liquid crystals and others.

A final note to my contribution to teaching may be added. Through my initiative Visiting Professors to the Faculty were invited: *Peter Atkins*, Oxford, on "Interaction

between Electromagnetic Radiation and Matter", *Peter Diehl*, Basel, on "NMR and Liquid Crystals" and *Jacques Courtieu*, Orsay, on " Modern NMR Techniques and Studies of Chirality".

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