

Rendiconti Accademia Nazionale delle Scienze detta dei XL Memorie di Scienze Fisiche e Naturali 119° (2001), Vol. XXV, pp. 61-66

## CLAUDIO FURLANI\*

## A brief history of relations between Chemical Research and Synchrotron in Italy\*\*

First of all I wish to thank the organizers of this meeting, the Italian Embassy in Sweden and its scientific Attaché Dr. Roberto Galloni, the Italian Institute of Culture in Stockholm and the group of Swedish and Italian scientists who developed the idea and undertook the task of organizing this cherished opportunity for a representative group of experts to discuss present-day developments in the area of synchrotron radiation. This area offers today the most promising and powerful methodologies known nowadays for the solution of fundamental problems both in physics and in chemistry by means of a generalized approach that is truly interdisciplinary and goes beyond the traditiona borders betwen physics, chemistry and other branches of the science of matter.

I am here not only personally as one of the researchers in the field where I have worked for more than twenty years, but also as a representative of two other official Italian organizations which have been, and still are, active in the promotion of synchrotron research and which have contributed financially, although only with limited amounts, to the organization of the present workshop: the Italian National Academy of Sciences known as the Fourty, a minor but important Academy besides the larger National Academy of Italy, which is the more well known Academy of the Lincei. The Academy of the Fourty has, however, a specific tradition of contacts with Sweden since it has a permanent collaboration agreement with the Royal Swedish Academy of Sciences, one of whose tasks is to organize yearly in alternate countries a series of international lectures given the names of Guglielmo Marconi and Jons Jacob Berzelius respectively, two symbol representatives of science in the

<sup>\*</sup> Uno dei XL. Dipartimento di Fisica «E. Amaldi», Università di Roma Tre, Via della Vasca Navale 84, 00146 Roma.

<sup>\*\*</sup> Lecture hold during the Swedish-Italian Workshop on Synchrotron Radiation: «Experiment and Theory», December 7-8, 2001, Stockholm, Sweden.

two countries, who happened to be both members of those two Academies. The last lecture of this series was given about two months ago here in Stockholm by Maurizio Cumo, one of our best experts of industrial safety and related problems. Therefore, the present workshop is not an isolated single initiative, but finds its place in a long traditional series of mutual exchange and collaboration between Swedish and Italian science. The other Italian institution I would like to mention is the Department of Physics of my University, the Third State University of Rome, which has the distinctive characteristic of having probably the highest density of synchrotron-dedicated people among all Italian university departments: four of us are indeed present here.

So far for the introductory remarks. Coming to my talk, I do not propose, as you may have seen from the program, to present a typical scientific report on specific items, but rather a few historical considerations on problems which are casting their long shadows on today's problems, and eventually to give also some information on our present problems and projects in Italy having a significant content of chemical nature, although definitely interdisciplinary as a whole. Again, I shall not present full scientific accounts, but just what I think will be sufficient to give you an idea of the chemical inspiration underlying our choice of synchrotron research problems.

I must say that connections between chemical research and synchrotron activity have not been intense in the past in Italy, and have started only relatively late. Today the situation is decidedly better, not only from my personal viewpoint but also from objective evidence as we have systematic synergies with physical research where many problems of chemical nature, having their roots in the in-house activity of chemical research groups find attention and proper treatment at synchrotron plants. However, it has not always been so in the past up to a few years ago. The profound reason for such a situation lies undoubtedly in the official organization of scientific research in Italy where, traditionally, there were sharp operative and financial distinctions, may I say borders or even fences, between different branches of science. So, chemists had their own organization, financements and closed development perspectives (a sort of scientific apartheid, if you like). Physicists had equally their reserved domains, and so had biologists, mathematicians and so on. Clearly, such a situation did not encourage chemists to look for contacts and collaboration with other scientists nor for search for novel techniques and methodologies. A further unsatisfactory aspect was that chemists were traditionally trained to use instruments as mere research tools, without interest nor ability nor specific formation for innovation in the field of instrumentation research. The common use was to buy instruments which promised good performances and use them in a automatic way to obtain the answers to our questions, which is almost the exact contrary of synchrotron research, where instrumentation is new, experimental in character and subject to continuous evolution, and requires of course a quite different attitude. Fortunately enough, there has been a number of young chemists

who became autonomously and spontaneously aware of the limitations implied in such an organization of official science and understood the need for a much wider synergy with other branches of research, first of all with the physics of matter. These young chemists also understood the necessity for a change in scientific formation and mental attitude toward opportunities and progress in instrumental research. Thus some bridges began to be built between chemical research groups and synchrotrons, or physical research groups working at synchrotrons, whereby it turned out immediately how useful such synergies could be in both directions, revealing to chemists the opportunity of using far more poweful methodologies and instrumentations, and helping physicists to better understand some chemical aspects of their problems. So now the situation is definitely improving, but again I must stress that such improvements are due more to individual, somewhat isolated initiatives of single research groups or sectors rather than to an ordered, large-scale planning backed by appropriate financial contributions by our national financing bodies. It is true that there has recently been some form of increased interest from our Ministry of Research, some National Research agencies such as the Italian Council of Research (CNR) and the National Institute for the Physics of the Matter (INFM). However, chemists still have no central organization of their own for planning, coordinating and financing their synchrotron radiation studies; our normal route to financement is either to submit applications for financement to our Universities or to our Ministry, which may or may not result in financial support (and only in a scattered, irreproducible and often quantitatively inadequate way) or join other national research organizations, where chemical research plays only a minor role but where it can count at least on the goodwill and the collaborative attitude of the host organizations. Along this line, the most efficient and satisfactory connection of chemical research is with the National Institute for the Physics of the Matter, where a chemical component is willingly accepted and supported, particularly in view of some problems and trends which are of equal or comparable interest from the viewpoints of both physics and chemistry. Other powerful links helping chemistry come out of its tendency to isolationism are represented by developments in modern materials science and by the big problems of present biology. As a matter of fact, these problems strongly call for an integrated participation of what was once pure chemistry, or pure biology, or specialized engineering. Nevertheless, some fundamental aspects of the organization of chemical research using synchrotron facilities are still waiting for a generalized solution. It must be mentioned that in Italy, as yet, there is no National Center which may take care of the links connecting local chemical research units dealing with basic chemical problems and synchrotron-dedicated or synchrotron-expert chemical researchers, and also support chemical research activities. We have a National Institute for Materials Science and Technology (INSTM, in practice a sort of National Institute of Chemistry) which may take care of these problems, were it not for the fact that it was founded only a couple of years ago and enjoys, or suffers, from too limited public financement to be able to play a leading role, or even use limited funds for chemical synchrotron research. Also, in Italy there is a Scientific Society for Synchrotron Light (SILS), where all branches of science, including chemistry, are present on an equal basis and which undertakes several valuable promotional activities. However, it is a purely scientific society with little or no financial income. Therefore, it cannot support research projects, but only schools, meetings and provide small prizes or financial contributions to promising young beginners.

Take for instance my personal history. I was born, scientifically speaking, as a typical chemist. I was rather good at boiling, crystallizing, producing bad smells, and at doing all those activities that are generally regarded as typical of chemists. Quite soon, however, I began to feel unsatisfied of synthesizing substances and I started to feel the need for a wider knowledge of their intimate nature and properties. By what means? At the beginning, I thought electrochemistry could be a good way to learn something about how electrons behave and are transferred in the course of chemical reactions. This is indeed true in part, but it does not lead to full solutions of structural problems: electrochemistry gives a lot of useful information, but does not give a full account of the whole of electronic molecular structure. Consequently, I went over to another methodology, i.e. spectroscopy. At that time, and I am speaking of more than twenty years ago, spectroscopy meant just electronic absorption spectroscopy in the visible and near ultraviolet, i.e. transitions between bound states, and even within those limitations it was able to rationally explain and classify some fundamental properties depending on electronic structure which had been until then left unexplained. Actually, for some time, ligandfield theory was the new frontier in inorganic chemistry, particularly for coordination compounds, and undoubtedly allowed brilliant and significant advances. In a later stage, however, it became evident that also visible-UV spectroscopy had its limitations for at least two reasons, one practical and one of principle. The former is that computations on inner shell transitions are very complicated, roughly approximate and yield rather bad comparisons between experiment and theory unless one is willing to undertake very complicated computations including all possible configuration interactions, relaxation and correlation effects. The second reason is that transitions to the external continuum, i.e. ionization transitions, which were rather neglected until then, were far more promising for a better and wider knowledge of electronic molecular structures. Therefore the next significant methodological step which drew my attention and efforts was the use of photoelectron spectroscopy (at that time, with traditional sources, i.e. X-ray tubes for solid samples, and gas discharge lamps for gaseous samples and single molecules). This was really a major turning point for chemistry as it offered for the first time the opportunity for concrete experimental measurements of charge distributions in solids (from chemical shifts of the binding energies of inner-shell atomic orbitals perturbed by their chemical environments), and for the experimental counterpart of the concept of molecular orbitals. These latter had been and still are a fundamental idea of structural chemistry, generally accepted as sound and safe, often

supported by indirect chemical evidence but which were still lacking, at that time, the direct experimental proofs which photoelectron spectroscopies made available later on. Thus for some years I enthusiastically dedicated my activity to photoelectron spectroscopy as applied mainly to inorganic chemistry problems. The next, and for the moment, final step came when we realized that photoionization with conventional sources was not the top and that it could be enormously improved by the use of synchrotron light of second or third generation which, other than ensuring much better resolution and intensity, offers the possibility of tuning the energy of ionizing radiation over rather broad ranges, thus adding a new dimension to the experimental capability of the technique, and even allowing the invention of several other derived or related new techniques. This is how I came to my present interest in experimental synchrotron research. Needless to say, new experimental possibilities lead to new challenges and developments in theoretical methods and applications, and vice versa, triggering a fruitful push-pull mechanism in the competition between theory and experiment.

As I told you before, I do not intend to present here a full account of synchrotron activities of the chemical type carried out at present in Italy. Since we have no central organization of our own for planning and coordinating chemical synchrotron research, it would be just a list of separate topics and, as such, of little significance. However, I promised to show you at least something concrete and, by way of example, I am going to show you some aspects of the present activity of my own research group at the Elettra synchrotron in Trieste. The long-range objectives of my minimum-size group, represented by myself and my direct collaborator Monica de Simone with the theoretical support of Piero Decleva, who is present here, essentially comprise an approach to the characterization by photoelectron spectroscopy of volatile metal compounds in order of increasing molecular complexity with particular attention to the role of atomic or pseudo-atomic d-type orbitals. Our program starts with a study of core and valence states of a series of quasi-isoelectronic pseudotetrahedral transition metal oxohalides TiCl<sub>4</sub>, VOCl<sub>3</sub>, CrO<sub>2</sub>Cl<sub>2</sub> and MnO<sub>3</sub>Cl, which are all closed shells; the next step would be some simple representatives of analogous open-shell systems, the simplest of which will be VCl<sub>4</sub>, similar to TiCl<sub>4</sub>, but with one more unpaired d electron. From simple open-shell volatile complexes we plan to go over to more complicated ones until the most modern and rather complicated volatile d-molecules produced by the recent advancements in chemical synthetic techniques.

Other objectives are a refinement of the electronic structure of  $SnBr_2$ , a molecule we have already investigated in the past but which still offers some interesting problems connected with strong correlation effects in the outer-shell quasi-valence region. High resolution XAS will also be applied to study the carbon and oxygen K-edges in series of simple organic molecules like tetrahedral  $CX_4$  and derivatives, hydroxy- and carbonyl derivatives and a more detailed study of some special features in the spectra of molecular oxygen both in its fundamental state and in two of its excited states.

I will not insist on instrumental details, such as the scheme of the absorption cell, which was built to also allow measurements of absolute spectral cross sections, since you are certainly well familiar with such aspects already. Rather, I will give you some brief preliminary information on our present work, particularly on the spectra of TiCl<sub>4</sub>, VOCl<sub>3</sub> and CrO<sub>2</sub>Cl<sub>2</sub> (we have not started work on the fourth member of the series yet, the manganese compound MnO<sub>3</sub>Cl, which is more difficult to handle experimentally. It is not actually explosive by itself, but some of its decomposition products are). These works were done also in collaboration with other researchers of the Elettra team, whose names I am going to mention in a moment. We now have full absorption spectra of the 3p and 2p edges of the three metals, of the 1s edges of oxygen and of the 2p edges of chlorine followed by PES spectra of Cl2p, Ti and V2p, O1s and outer and inner valence orbitals of the titanium and vanadium compounds (in this initial stage PES spectra were taken at the magic angle, i.e. without angular resolution; angular resolved spectra and the determination of asymmetry parameters can be achieved with our instrumentation, and will actually be our first goal for the near future).

I think I can say that our original expectations are satisfactorily fulfilled as our experimental material is of good quality and shows good resolution and evidence for several new and sometimes unexpected features such as satellites, weak absorptions, extra bands and multiplet resolution. Moreover, already these relatively simple systems reveal in practice unexpected experimental and interpretative difficulties; we are still far from a satisfactory coverage of all involved electronic and spectroscopic aspects despite intense and accurate experimental work and achievement of several significant new results. If we can draw a partial and temporary conclusion from the admittedly scarce and unfinished experimental material gathered so far, it is that all previous works done on these and other relatively simple molecules have to be completely revised, and will probably reveal a great many significant new data. These latter will widen our knowledge of such systems to a considerably higher level and, at the same time, will require renewed efforts from our theoretical friends to cope with the new experimental findings.

In the end, let me mention the names of other members of the staff of the Gas-Phase Beamline at the Elettra Synchrotron in Trieste we are collaborating with not only on the problems I have just presented, but also on several other research projects which are included in the vast agenda of the Gas-Phase Beamline in Trieste. These other research projects will be better illustrated by Kevin Prince, who is one of the next speakers. In particular, I would like to mention and thank ,besides Kevin Prince, Monica de Simone, Piero Decleva as well as Marcello Coreno, Pietro Franceschi, Giovanna Fronzoni and Sara Furlan.

As I have anticipated at the beginning of my talk, I have presented only partial and limited scientific results, and more of historical and critical considerations. Consequently, please consider this initial talk of mine as a sort of a journalist report from Italy, and let me wish this workshop the best success for its scientific continuation.