Rendiconti
Accademia Nazionale delle Scienze detta dei XL
Memorie di Scienze Fisiche e Naturali
136° (2018), Vol. XLII, Parte II, Tomo II, pp. 7-15

VINCENZO AQUILANTI*

The Astrochemical Observatory: Chemistry in the sky

Summary – The sixteen chapters of this book are a collection of short essays and extended abstracts, which originated from presentations at an event that took place in 22 and 23 March 2018 in Villa Torlonia in Rome. The venue was the Library of the Accademia Nazionale delle Scienze detta dei Quaranta (National Academy of Sciences, known as of the Forty). The participants to the conference shared interest for the role of molecules in connection with the modern science of the Universe. The recent designation for this area of research goes under the name of Astrochemistry. A brief history of this discipline is sketched, with particular emphasis on the roots, namely the developments that took place back in time, essentially due to an eminent astronomer, Angelo Secchi: in the Nineteenth century he was known as "the Chemist of the sky": he was curious about the role of chemical elements in the observational data from his telescope, that he had equipped with a spectroscope. The nucleus of the group of scientists carrying out concerted efforts under the denomination "Astrochemical Observatory" operates since a dozen years: it is diffused in various universities and research centers essentially based in central Italy, extended to collaborators in the Nation and abroad. The theme chosen for this year's event that can be considered as one of a series, is molecular chirality, a topic transversal across many disciplines that has relevance also for evolutionary sciences. The conference was dedicated to the memory of Giangualberto Volpi, the founder of a school in chemical kinetics who had died in February 2017: in June 2018, he would have been ninety years old: Volpi's school was based first in Rome on ion-molecule reactions and then in Perugia on neutral reactions. A member of his school, Anna Giardini who later contributed to the topic of chiral recognition, was the special guest of the conference. Anticipations are indicated of future meetings: the one in 2019 will be devoted to chemical kinetics, while other events in preparation will be centered about the figure of Primo Levi, writer, chemist, prominent figure, protagonist of the cultural debate of last century, in occasion of his one hundredth birthday.

* One of the XL – Dipartimento di Chimica, Biologia e Biotecnologie, Università di Perugia, 06123 Perugia, Italy. Consiglio Nazionale delle Ricerche, Istituto di Struttura della Materia, 00016 Roma, Italy. E.mail: vincenzoaquilanti@yahoo.it

Opening the March 2018 event

The call for the present conference had the goal of establishing a starting event for an initiative involving research groups in Italy active in carrying out projects in astrochemistry. The melting pot consisted of a scientific reunion assessing the state of the "Astrochemical Observatory", that had been formalized in 2016 under the auspices of the Italian Accademia Nazionale delle Scienze detta dei XL (National Academy of Sciences, known as of the Forty). The initiative is regarding wide areas covered by the emerging science going under the name of astrochemistry – a new name with an immediate self-explaining connotation. To this theme, several activities had been dedicated already in the recent past, and the particular focus of this gathering has been centered around that of molecular chirality. However, the occasion was taken of extending the presentations to related topics, in order to give an account of the general status of the research in this field from Italian scientists, enlarged to their principal international collaborators. For an account published in 2012 of the preliminary proposals see Figure 1.

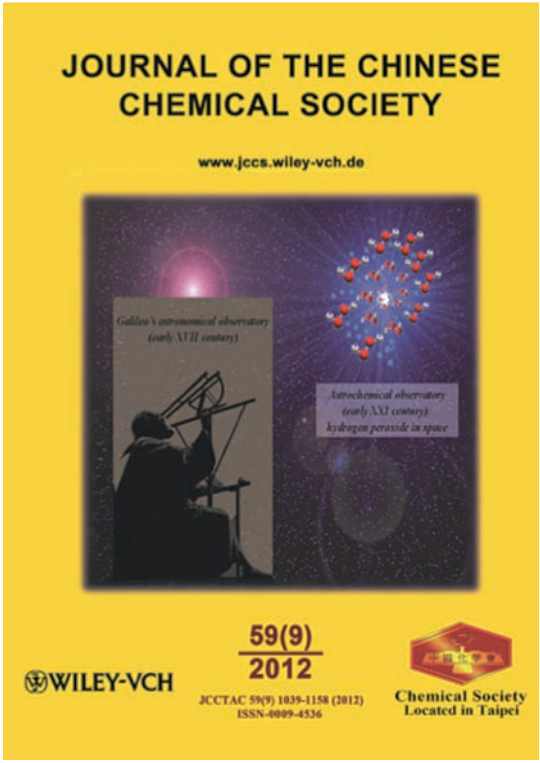

Fig. 1. Cover of the Journal where in 2012 an article on the Astrochemical Observatory project was presented, with particular emphasis on the collaborations with Osaka and Taipei laboratories.

Twenty years ago in Rome…

The First European Workshop on an emerging discipline "Exo-Astro-Biology", took place in Frascati, near Rome, in 2001 and included the attendance of many chemists. Proceedings are available (see Figure 2): the concluding sentence of one of the progress reports (Keheyan *et al.* 2001) refers to "astrobiological implications of our laboratory discovery, the detection of aligned benzene in gaseous streams (see the Physical Review Focus, http://focus.aps.org.no.26,29 May 2001, and Chemical,

Fig. 2. The proceedings of the First European Workshop on Exo-/ Astro-biology in 2001.

Engineering News, 11 June 2001, p. 22) and previous evidence on simpler molecules point out that as our future work plan we focus on possible mechanisms for chiral bio-stereochemistry of oriented reactants, for example when flowing in atmospheres of rotating bodies, specifically the planet Earth". A decade later, at the 2010 and 2012 Rome Lincei Conferences on Astrochemistry and Chirality, respectively, the opportunity was provided of presenting an account of the progress regarding that initial proposal.

The search for possible stereodynamical mechanisms of chiral discrimination based upon collisions, involves design of new experiments and the laboratory techniques must be upgraded to distinguish between enantiomers. This objective requires sharpening not only the experimental tools, but also the theoretical ones provided by modern physical chemistry (Aquilanti *et al.* 2008): quantum and semiclassical approaches developed for few-atom reactions need extensions to cases of more complicated many-body systems to explicitly include chirality, starting by defining convenient parametrization of chiral observables for enantiomeric distinguishability. From an experimental viewpoint, progress continues to be required on collisional alignment in gaseous streams and on various aspects of physicochemical sciences, aimed at understanding spatial aspects of molecular structure and dynamics. The main target here is to measure and/or to calculate crucial kinetic parameters (cross sections and rate constants) to be used in models to verify the hypothesis that molecular collision mechanisms can induce chirality discrimination. Experiments involving molecular beams techniques, assisted by model molecular dynamics calculations, are currently being performed and described in some of the papers collected here.

The prequel: Angelo Secchi, the chemist of the sky

The Nineteenth Century Jesuit Angelo Secchi (Reggio Emilia 1818 – Rome 1878) was defined as "the chemist of the sky". He was very well known in his times for many scientific contributions and discoveries: not only he was an astronomer and an astrophysicist, but also established important geophysical benchmarks, such as the definition of the Rome meridian, and laboratory studies of the Earth magnetism and of meteorology. Regarding his contribution to astronomy, during the several years when he acted as the director of the Pontifical Observatory, he had implemented the idea of adding a spectroscope to his telescope and in this way he could follow the "royal road" established by Fraunhofer and others. Importantly, he was the first to focus not only on the spectral lines (which were correctly attributed to atomic spectra) but also to bands, which were subsequently associated to molecular spectra. In this sense he was really doing chemistry. Additionally, one of the main aspects of the great fame of Secchi came when he classified stars according to their chemical compositions: his classification was the first to be proposed and lasted as the standard one for few decades, until the British classification modified his approach by substantial variants.

Angelo Secchi was a member of the Academy of the Forty and was a Jesuit: his laboratory was placed in central Rome at the roof of the S. Ignazio church, which is the headquarter of the Jesuit Order. Unfortunately for him, when in the Seventies of the XIX century, Rome passed from the Pontifical Reign to the newly formed Italian Kingdom, Father Secchi, as functionary of the Papal state, was under scrutiny for removal by the new state and for dismission from his position as Chief Astronomer. The Italian Senate voted by a tiny majority in his favor and for him to continue to be the head of the Observatory, especially thanks to the influence of Quintino Sella – then Minister of Economics of Italy and the president of the newly reorganized Lincei Academy. The Pope established an alternative a new branch of the academy, known as Accademia Pontificia, and Secchi was as appointed the president of it. Exceptionally, he was allowed to continue his activity as Chief Astronomer until his death in 1878. He was a member of the Academy of the Forty, without interruption from 1858 to 1878: to celebrate him, the Academy organizad an important meeting on the occasion of his centennial anniversary: the proceedings of this conference were published in 1979 and a second edition was printed in 1993. In the year 2018 in September, a conference subsequent to the present one, celebrating the bicentennial of his birth, took place: a stamp was issued from the Italian Mail (Figure 3) and proceedings are being prepared from the Academy of the Forty also on this event.

Fig. 3. Celebration of Angelo Secchi (the Chemist of the sky), on the Bicentennial of his birth, by a postcard and a stamp from the Italian Mail in April 2018.

A dedication: Giangualberto Volpi and chemical kinetics

The conference is dedicated to professor Giangualberto Volpi (Figure 4), who died exactly one year before this event in February 2017 and would be ninety-year-old at the time of writing. To his memory, a commemorative article appeared in this Rendiconti, Aquilanti, 2016. He belonged to a team that in the post-war Italy started a pioneering activity on elementary chemical reactions, innovating the instrumentation of chemical physics by introducing the first especially built mass spectrometer in the country, homemade in the laboratory of professor Giorgio Careri in the Physics Institute of the University of Rome. The instrument was essential for a kinetic study of the prototype of all chemical reactions, the isotopic exchange of hydrogen and deuterium, and that work provided the first convincing experimental confirmation of Transition State Theory, which had been formulated about 25 years before by Eyring, Polanyi, Wigner. In successive decades, Volpi established a research activity in the General Chemistry Institute in the University of Rome, devoted to elementary chemical processes, innovating the scope of investigations of the group to the point that it is now recognized as among the first teams to study physics and chemistry involving ions by high pressure mass spectrometry. The group became soon a world leader on ion-molecule reactions, and the results obtained were considered of main interests in radiation chemistry and in the chemistry of plasmas, with applications to the ionosphere research and more recently to astrochemical environments. In fact, well beyond the expectation of scientists of the atmospheres of the planets in the solar system, ion-molecule reactions are being considered as playing an important role even in discussions of the early Universe, regarding the formation of atoms and molecules through reactions of ions. The book reports articles on these and related topics.

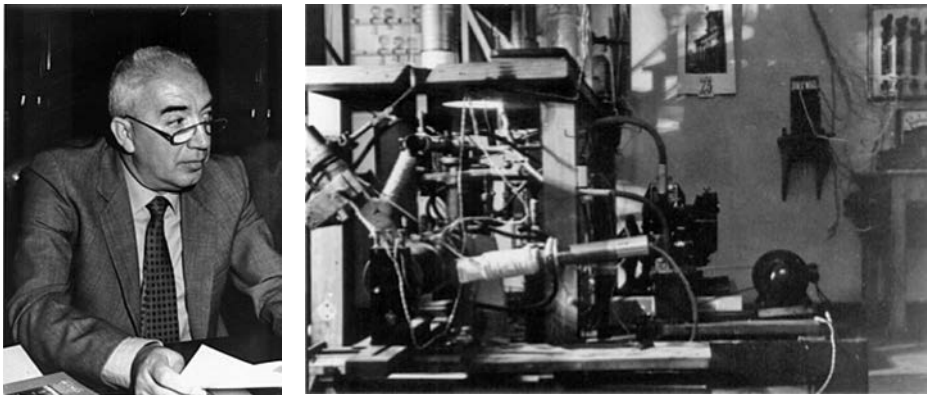

Fig. 4. Gian Gualberto Volpi in his office in Perugia at the beginning of the century. Also shown the mass spectrometer of the Fifties.

Special guest: Anna Giardini and chiral recognition

Anna Giardini's work was recognized worldwide as that of a fine experimentalist with a deep involvement in studying processes of relevance both to theoreticians and to applied scientists. Her enthusiasm and tireless energy were so well known that it is no surprise to us that after retirement from the University she had been still active in the National Research Council Laboratories. As a further impressive demonstration of the ample spectrum of interest that have characterized her scientific career, she more recently focused on the study of ultrafast photophysical and photochemical processes with femtosecond lasers, performing pump-probe spectroscopy experiments of molecules of biological relevance in liquid solutions. Important are her contributions to chirality issues, see Figure 5 and many articles in this book by her former collaborators and students.

Fig. 5. Anna Giardini in her office at La Sapienza of Rome around 2005. Several contributions in this collection come from her main coworkers on chirality issues, such as Professor Maurizio Speranza, and former students Susanna Piccirillo, now at the University of Rome Tor Vergata, Daniele Catone and Mauro Satta, now at CNR, the Italian National Research Council, and others.

The sequel: Primo Levi, chirality and the periodic system

The year 2019 is the centennial of the birth of Primo Levi who was a chemist both as training (doctor in Chemistry in Turin in 1941) and for many years also by profession. Any intent to highlight the significant role in his life and in his work of science (and of chemistry in particular), is often overshadowed by the immense notoriety of his great figure as narrator and witness of his time. The famous book by Levi *Il Sistema Periodico*, "The Periodic System" (1975), see Figure 6, is a paramount

Fig. 6. The first edition of one of Primo Levi's narrative masterpieces, and one where the "fil rouge" is the reference to his chemical background. Note the cover, by a drawing by M. S. C. Escher, showing a three-dimensional paradox inspired by a Möbius band: to the early XIX century mathematician Möbius the geometrical concept now known as chirality is attributed.

example of narrative writing inspired and permeated by scientific philosophy. Additionally, the year 2019 marks the 150th anniversary of the formulation of the periodic system of elements by Medeleev: this milestone was celebrated ten years ago in an interdisciplinary Lincei congress and updates are proposed also in reference to the work of Levi. In Levi, the theme of molecular chirality pervades his writing explicitly or as a metaphor: in future events, presentations of this interdisciplinary theme will also be addressed.

In 2017, the Italian Chemical Society, together with the German counterpart, instituted the two-year Primo Levi Prize and awarded the Nobel Prize laureate Hoffmann with a prestigious ceremony, held in Germany, that has been given a great deal of attention from media. The next award will be organized by the Italian Chemical Society in Rome in December 2019: accompanying events are being planned emphasizing highly interdisciplinary features

As mentioned, Primo Levi was a chemist by profession, his doctoral dissertation concerned Walden's inversion, related to chiral changes: he later published a famous article on molecular chirality and asymmetry of life, whose relevance was underlined by the physicist Tullio Regge, with whom he discussed in more occasions about the possible dialogue between the two cultures. The title of one of his collections is *L'Asimmetria e la Vita* (Asymmetry and Life). The excellence of his

writing pervades his literary works, as a witness to the Holocaust, as a publicist, as a scientific disseminator within narrative contexts, transcending the barriers between the "two cultures".

Concluding the presentation of the book dedicated to the 2018 event, it is an appropriate signal towards the future to indicate that dates and location for the next event, OAK – Observatory for Astrochemical Kinetics, are already settled: again Rome, the Biblioteca dell'Accademia dei XL, 27 and 28 June 2019: old and new participants are cordially invited to joint efforts on the current and future chemical themes inspired by the surprising discovery of myriads of planets outside the Solar System.

BIBLIOGRAPHY

Aquilanti V., Molecular and Nanodynamics: from atoms to biomolecules, 2008. Physica Scripta, 78, 050301.

Aquilanti V., Piccirillo S., Speranza M., Anna Giardini's journey from atoms to biomolecules, 2008. Physica Scripta, 78, 050401.

Aquilanti V., Grossi G., Lombardi A., Maciel G. S., Palazzetti F., 2008. The origin of chiral discrimination: supersonic molecular beam experiments and molecular dynamics simulations of collisional mechanisms. Physica Scripta 78,058119-058125.

Aquilanti V., Grossi G., Lombardi A., Maciel G.S., Palazzetti F., 2011. Aligned molecular collisions and a stereodynamical mechanism for selective chirality. Rend. Fis. Acc. Lincei 22,125-135.

Aquilanti V., 2016. Ricordo di Gian Gualberto Volpi. Rendiconti Accademia Nazionale delle Scienze detta dei XL, Memorie di Scienze Fisiche e Naturali 134° Vol. XL, Parte II, 45-49.

Boato G., Volpi G.G., Experiments on the Dynamics of Molecular Processes: A Chronicle of Fifty Years, 1999. Annual Review of Physical Chemistry, 50, 23-50.

Keheyan Y., Aquilanti V., Brucato J.R., Colangeli L., Cataldo F., Mennella V., 2001. Astrochemical and prebiotical elementary processes. In: European Workshop on Exo-/Astrobiology, Frascati, May 2001, esa SP, August 2001, pp. 357-361.

Palazzetti F., Maciel G.S., Lombardi A., Grossi G., Aquilanti V., 2012. The astrochemical observatory: molecules in the laboratory and in the cosmos. J. Chin. Chem. Soc. 59, 1045-1052.

Secchi A., Sugli spettri prismatici delle stelle fisse, 1867. Rendiconti Accademia Nazionale delle Scienze detta dei XL, 67-152.

Secchi A., Sulla grande nebulosa di Orione, 1868. Rendiconti Accademia Nazionale delle Scienze detta dei XL, 99-134.

Secchi A., Sugli spettri prismatici delle stelle fisse, Memoria Seconda, Pubblicata nel 1869/1876 Rendiconti Accademia Nazionale delle Scienze detta dei XL, 73-133.

Secchi A., Sugli spettri prismatici de' corpi celesti, Memoria Terza, Pubblicata nel 1869-1876. Rendiconti Accademia Nazionale delle Scienze detta dei XL, 191-248.