

# The fifth chemical revolution: 1973–1999

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**Abstract** A new chronology is introduced to address the history of chemistry, with educational purposes, particularly for the end of the twentieth century and here identified as the fifth chemical revolution. Each revolution are considered in terms of the Kuhnian notion of 'exemplar,' rather than 'paradigm.' This approach enables the incorporation of instruments, as well as concepts and the rise of new subdisciplines into the revolutionary process and provides a more adequate representation of such periods of development and consolidation. The fifth revolution developed from 1973 to 1999 and is characterized by a deep transformation in the very heart of chemistry. That is to say, the size and type of objects (substances), the way in which they must be done and the time in which they are transformed. In one way or another, chemistry' limits had been set out.

**Keywords** History of chemistry · Chemical revolutions · Chemistry education · Exemplars · Instruments and subdisciplines

# Introduction

In spite of the impressive growth and qualitative change of science over the last half century, however, historians of science still largely turn their attention to earlier periods. Thus a paradoxical temporal imbalance is created: one the one hand, the great majority of historians of science are still working on the small percentage of scientific activity

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*that took place before 1945.* Söderqvist (1997, p. 3)

Historians of science and chemistry teachers show little attention to modern chemistry.<sup>1</sup> However, chemistry changes and had changed throughout its history. The explanation of science's change and development over time has been the subject of various proposals both historically and philosophically.<sup>2</sup> Of all stands that of Thomas Kuhn, whose book The Structure of Scientific Revolutions is a milestone for those interested in the construction of scientific knowledge. His ideas about scientific revolutions have been widely accepted. For him, scientific revolutions are (1970, p. 92): taken to be those non-cumulative developmental episodes in which an older paradigm is replaced in whole or in part by an incompatible new one. This change requires the reconstruction of the commitments of a particular scientific community along history. The commitments shared by groups or communities are recognized through the use of the word 'paradigm' that means (1970, p. 37): a criterion for choosing problems that, while the paradigm is taken for granted, can be assumed to have solutions. Different scientific communities share over the same historic period the same paradigm and around it they perform their research doing "normal science". When there is a scientific revolution the community changes its paradigm changing activities related to 'normal science'.

Kuhn's 'paradigms', 'incommensurability' and 'revolutions' have been deeply studied and challenged<sup>3</sup> as has his lack of interest in technology.<sup>4</sup> That is to say from the very beginning Kuhn was criticised for his vague concept of paradigm and for using it, at least, in 22 different ways. Kuhn himself accepted this criticism and in his Postscript to the 1970 edition of *The Structure of Scientific Revolutions* he indicated that he had conflated two conceptually distinct connotations of paradigms-'exemplars' and 'disciplinary matrices'<sup>5</sup>:

(...) [b]ecause the term [paradigm] has assumed a life of its own... I shall here substitute 'exemplars.' By it I mean, initially, the concrete problem-solutions that students encounter from the start of their scientific education, whether in laboratories, on examinations, or at the ends of chapters in science texts....All physicists, for example, begin by learning the same exemplars: problems such as the inclined plane, the conical pendulum, and Keplerian orbits; instruments such as the vernier, the calorimeter and the Wheaststone bridge (Kuhn 1970, p. 187).

<sup>&</sup>lt;sup>1</sup> See for example: Söderqvist (1997), Chamizo (2014), however an exception is Cerruti (2016).

<sup>&</sup>lt;sup>2</sup> See for example: Bachelard (1979), Bernal (1971), Laudan (1977) and Pickstone (2000).

<sup>&</sup>lt;sup>3</sup> See for example: Cohen (1985), Gutting (1980), Hoyningen-Huene (2008), Kindi and Arabatzis (2012), Lakatos and Musgrave (1970), Rouse et al. (1998) and Toulmin (1972).

<sup>&</sup>lt;sup>4</sup> Indeed technology is almost unique among disciplines in having been the subject of only the occasional Kuhnian analysis. There are, I believe, three reasons why this has been so: first, the assumption that technological knowledge is quintessentially tacit; second, the identification of technological knowledge with applied science; and third, the selection of analytical units for the history and present structure of technology that, however useful, for some purposes, do little to throw the cognitive aspect of technology into prominence. During the past decades or so, a number of different developments in the study of technology have been made these barriers less formidable than previously" (Laudan 1984, p. 6).

<sup>&</sup>lt;sup>5</sup> The disciplinary matrix contains; symbolic generalizations, methodology, values and exemplars (Marcum 2012).

Thus, the term 'exemplar' represents a specific historical community's collection of solved problems and it is generally found in its professional literature, and especially in its textbooks. It is narrower than paradigm<sup>6</sup> and avoids some of the ambiguities that the latter has acquired. Making explicit the role of instruments in normal science reduces the gap between normal and revolutionary science. This has an important consequence, because exemplars, being more flexible and also more practically accurate than paradigms, not only recognize the conceptual or theoretical changes within a discipline, but also indicate that they are accompanied by the design,<sup>7</sup> construction and use of certain instruments.<sup>8</sup>

Following what was discussed at previous papers (Chamizo 2011, 2014), here I will develop what I have called The Fifth Chemical Revolution (1973–1999), where three new instruments: electron capture detector; flash photolysis with Ti–sapphire laser beam and the scanning tunneling microscope, and major improvements in NMR and X-ray crystallography, changed the way of seeing and understanding chemistry, and the concepts that were developed with them as the new subdisciplines that emerged appeared throughout this period: green, organometallic, supramolecular, nano and femto chemistry.

#### **Exemplars and revolutions**

Nothing tends so much to the advancement of knowledge as the application of a new instrument. The native intellectual powers of men in different times are not so much the causes of the different success of their labors, as the peculiar nature of the means and artificial resources in their possession. Sir Humphry Davy (1812)

Challenging the common idea that science is fundamentally theory, in the last decades no one has contributed more than the Canadian philosopher Ian Hacking to articulate the variety of roles that experiments play in the production of knowledge. In *Representing and Intervening* he recognized that much of our empirical knowledge results from interventions with instruments. Only by intervening it is possible to discover the material resistances of the world.<sup>9</sup> His phrase has become a breakpoint: *Experimentation has a life of its own*,

<sup>&</sup>lt;sup>6</sup> The original Kuhn paradigm has two meanings: wide as disciplinary matrix and narrow as exemplar (Kindi and Arabatzis 2012).

<sup>&</sup>lt;sup>7</sup> Dyson (1999) recognized that astronomers and biologist have different attitudes towards their instruments. Astronomers traditionally invented and built their own instruments...and biologist buy them.

<sup>&</sup>lt;sup>8</sup> Here is important to recognize the words of Gary Gutting, one of Kuhn's critics: One instance is technological practices that exist independent of theoretical science (arts and crafts). In contrast to the common view that such practices are entirely unscientific, being at best instances of knowing how rather than knowing what, an analysis in terms of exemplars suggest that both the skilled artisan or craftsman and the pure scientist are in essence people how know how to adapt and extend previously exemplary achievements to new cases (Gutting 1984, p. 56).

<sup>&</sup>lt;sup>9</sup> As Boon recently indicated: According to Hacking, we invent devices that produce data and isolate or create phenomena, and a network of different levels of theory is true to these phenomena. Conversely, we may in the end count them as phenomena only when the data are interpreted by theory. Thus there evolves a curious tailor-made fit between our ideas, our technological instruments, and our observations, which Hacking calls coherence theory of though, action, material things, and marks (Boon 2015, p. 64).

interacting with speculation, calculation, model building, invention and technology in numerous ways (Hacking 1983, p. xiii). For him the epistemic grounds for belief in an invisible entity, like electrons, come not from the theory underneath, but from the ability to manipulate it (1983, pp. 22–24): *If you can spray them, then they are real*... This separation between theory and experiment and yet his obvious immediate vicinity is evidenced when there is a 'theoretical' paradigm shift. As pointed out by Stephen Toulmin, many years ago:

If we are to make the theory of paradigms and revolutions fit the actual historical evidence, accordingly, we can do so only on one condition. We must face the fact that paradigm switches are never as complete as the fully-fledged definition implies; that rival paradigms never really amount to entire alternative world-views; and that intellectual discontinuities on the theoretical level of science conceal underlying continuities at a deeper, methodological level (Toulmin 1972, pp. 105–106).

And that methodological level is no other than that referred to the use of instruments.<sup>10</sup> The use of new instruments<sup>11</sup> opens new territories sometimes without having any underlying theory. This connection between words and things, concepts and instruments can acknowledge, more clearly and comprehensively, the activities that constitute a specific scientific community, in a particular historical moment (Rouse et al. 1998). Thus, such a seemingly simple concept such as temperature, that unlike length lacks a solid reference and which is measured through a specific instrument (thermometer), it is not so simple. As demonstrated by Chang (2004) stabilizing observations about certain phenomenon in the world, using instruments, requires consideration of a particular theory of operation.

As Xiang Chen wrote several years ago in his work about Kuhn's latest notion of incommensurability:

However, differing from linguistic factors, instruments always have lives of their own without necessarily being dominated by paradigm or theory. In addition to the guidance of theoretical knowledge, the development of instruments is also grounded in a material culture, which includes such non-linguistic factors as experimental techniques, procedures, skills, and expertise. In the history of science many instruments were in fact designed and built prior to the formulation of relevant theories, and the advancement of instruments (including the related techniques and skills) continuously shapes the formulation of theory (Chen 1997, p. 270).

<sup>&</sup>lt;sup>10</sup> For example Davis Baird claims that: *instruments are not in the intellectual basement; they occupy the same floor as our greatest theoretical contributions to understand the world* (Baird and Shew 2004, p. xvii). About this Yakov Rabkin standpoint: *Indeed the traditional emphasis historians of science have put on theory as the motor of scientific development tends to obscure the roles of instrumentation that are at the root of progress in chemical analysis. Consequently, the instrument has acquired the appearance of a tool manufactured expressly for the chemical investigator intent on making an ultimate breakthrough. This imaginary is related to the commonplace subordination of technology to science in much of the existent literature on the subject (Rabkin 1993, p. 26).* 

<sup>&</sup>lt;sup>11</sup> In their *Instruments of Science. An Historical Encyclopedia*, Bud and Warner indicated: "Scientific instruments are central to the practice of science. All too often they have been taken for granted. Nonetheless, while most would agree that telescopes and microscopes are scientific instruments, it has probed as difficult to establish a general definition of the category, as it has been to define science itself" (Bud and Warner 1998, p. ix).

So in recent years and from different traditions<sup>12</sup> has been recognized that instruments play a key role in the changes occurred in the development of sciences.<sup>13</sup>

In addition to the role of new instruments in generating significant changes in research and in the formation of new kinds of specialization, the role of the textbook in signalling the end of scientific revolutions was also clearly identified by Kuhn himself. At the end of his career he recognized a different meaning of incommensurability,<sup>14</sup> indicating that the emergence of new sub-disciplines within a discipline as a result of a scientific revolution, and accepted by new textbooks,<sup>15</sup> separated scientific communities (Kuhn 1992). Particularly, he recognized that incommensurability is important for the growth of scientific knowledge because it isolates practitioners' communities by creating communication barriers that promote the proliferation of specialities.<sup>16</sup> He also introduced the concept of lexicon to capture both a term's reference and intention or sense.<sup>17</sup> It other words, scientific revolutions can be characterized by:

<sup>14</sup> First, the episodes that I once described as scientific revolutions are intimately associated with the ones I've here compared with speciation. It's at this point that the previously mentioned disanalogy enters, for revolutions directly displace some of the concepts basic in a field in favour of others, a destructive element not nearly so directly present in biological speciation. But in addition to the destructive element in revolutions, there's also a narrowing of focus. The mode of practice permitted by the new concepts never covers all the field for which the earlier one took responsibility. There's always a residue (sometimes a very large one) the pursuit of which continues as an increasingly distinct speciality. Though the process of proliferation is often more complex than my reference to speciation suggest, there are regularly more specialities after a revolutionary change than there were before...The second component of the return to my past is the specification of what makes these specialities distinct, what keeps them apart and leaves the ground between them as apparently empty space. To that the answer is incommensurability, a growing conceptual disparity between the tools deployed in the two specialities. Once the two specialities have grown apart, the disparity makes it impossible for the practitioners of one to communicate fully with the practitioners of the other. And those communication problems reduce, though they never altogether eliminate, the likelihood that the two will produce fertile offspring (Kuhn 1992, pp. 19–20).

<sup>15</sup> As was indicated by Bernadette Bensaude-Vincent: Whereas historians of science ignored textbooks because of the gulf between producing science and communicating science, a number of philosophers of science have emphasized their importance due to this gulf... Thomas Kuhn also recognized the importance of textbooks for the stabilization and perpetuation of paradigms. Textbooks are fundamentally conservative as they are meant for training students in solving the puzzles raised within the paradigm rather than inventing new problems. Kuhn argued that they assume their conservative function through various ways. They present only established and incontrovertible knowledge, the stable results of past revolutions (Bensaude-Vincent 2006, p. 669).

<sup>16</sup> See for example, Law (1973).

<sup>17</sup> As Marcum recognized (2015, p. 138): Inconmensurability plays a critical role in scientific progress by providing an opportunity for a new lexicon to develop fully without interference from the parent lexicon.

<sup>&</sup>lt;sup>12</sup> In technoscientific research, the development of theories is often entangled with the development of instruments that produce technologically relevant phenomena (Boon 2015, p. 78). See also Agar (2012).

<sup>&</sup>lt;sup>13</sup> Some recent publications about this are: Pitt (2010) about engineering; Soler et al. (2013) about calibration; Boon (2015) about instruments themselves; about chemistry laboratories Morris (2016). Related to this discussion Peter Galison's book *Image and Logic* about twenty century physics, differentiate three layers, or levels, of this science: theory, experiment and instrumentation. Discussing the long-term stability of physics he recognized that there were breaks and revolutions, either in the instrumental, experimental or theoretical domains. The layers are intercalated and each one has different time' spans. Whereas one of them has disrupted, the structures of the other layers remain largely intact "When a radically new theory is introduced, we would expect experimental practices across theoretical breaks are now abundant in the new literature of experiment. For the first time there are a real interest in the dynamics of experiment outside the provision of data to induce, confirm, or refute specific theories" (Galison 1977, pp. 799–800). Related to this see Morris (2016).

A second, closely related, and equally fundamental role: they are often, perhaps always, associated with an increase in the number of scientific specialities required for the continued acquisition of scientific knowledge (Kuhn 1993, p. 336).

Allowing for specific historiographical variations among historians, the above considerations suggest that there are at least five acceptable answers to the question "What is a scientific revolution?" According to what has been said previously, these are:

- 1. A radical reinterpretation of existing thought recognized by contemporaries themselves.
- 2. The resolution of a long-standing debate, the solution of which revolutionizes the kind of problems scientists are able to successfully attack on a routine basis.
- 3. The use of new instruments changes<sup>18</sup> the way in which its practitioners look and work in the world.<sup>19</sup>
- 4. The opening of a new level of theoretical understanding that subsumes older theories as special cases.
- 5. The opening of new subdisciplines that produces separated scientific communities with their owns lexicons.<sup>20</sup>

Based on the above, history of chemistry can be divided into two main groups. The first that can be called "protochemistry" and the second "chemistry" with its five revolutions, each one characterized by instruments, concepts and the emergence of new subdisciplines, as can be seen in Table 1.

I have discussed previously in relation to the first three revolutions (Chamizo 2014), the period that can be identified coincides with what recently Ursula Klein called "classical chemistry". Using her own words:

Therefore, I'll restrict my paper to early modern and modern chemistry, say, from the early eighteenth century to the mid twentieth century. I neither include alchemy before ca. 1700 nor the late modern chemistry after ca. 1940. After ca. 1940 quantum chemistry was firmly established and physical spectroscopic instruments and methods of chemical analysis began to proliferate; these changes affected the key epistemological and methodological role played by material substances in all chemical fields until that time. I call the period and type of chemistry that replaced alchemy and predated late-modern chemistry the "classical chemistry" (Klein 2012, p. 8).

Footnote 17 continued

About the importance of lexicons Kuhn said: *Each community has a somewhat differently structured lexicon and each engages in a somewhat different form of professional life* (cited in Marcum 2015, p. 139).

<sup>&</sup>lt;sup>18</sup> On this account, *empirically a new instrument may open a new field of research* where there may be no theory to explain what it measures. As Kuhn noted, it then requires a period of time to assimilate and explain what happens (1970): *Many of the early experiments involving thermometers read like investigations of that new instrument rather than investigations with it. How could anything else have been the case during a period when it was totally unclear what the thermometer measured?* In this sense major refinements in the instruments are also significant.

<sup>&</sup>lt;sup>19</sup> Hasok Chang strongly supports pluralism in science. For him "In place of monism (the notion that science is the search for the truth about nature) I offer pluralism as an ideal of science. I would define pluralism in science as the doctrine of advocating the cultivation of multiple systems of practice in any given field of science. By a "system of practice" I mean a coherent and interacting set of epistemic activities performed with a view to achieve certain aims" (Chang 2012, p. 260). In agreement with this approach, here answer 3 must be always considered, but not exclusively.

<sup>&</sup>lt;sup>20</sup> If I were now rewriting 'The Structure of Scientific Revolutions', I would emphasize language more and the normal/revolutionary distinction less (Kuhn 1983, p. 715).

Revolution	Main instruments	Main concepts	Disciplines and subdisciplines
First 1756–1808	Pneumatic trough Balance Calorimeter	Language Quantitative chemistry Atoms	Chemistry
Second 1828–1869	Kaliapparat Polarimeter	Molecules Isomers Valence Periodicity	Organic chemistry
Third 1897–1923	Cathode rays tube Mass spectrometer	Electrons Nucleus, isotopes	Structural physical chemistry Nuclear chemistry
Fourth 1945–1965	Chromatograph EPR, UV, IR, <sup>1</sup> HNMR, X ray crystallography	Orbitals Spin	Instrumental analytical chemistry Molecular biology Theoretical chemistry
Fifth 1973–1999	Multinuclear FT NMR Electron Capture Detector Flash (lasser-beam) photolysis Scanning Tunneling Microscope	Hapticity, metal cluster compounds, fluxionality, ozone layer depletion, sustainability, atom economy, life cycle analysis, self-assembly, self-organization, crown ethers, cryptands, fullerenes	Organometallic chemistry Green chemistry Supramolecular chemistry Nano chemistry Femto chemistry

Table 1 The five chemical revolutions, characterized by some of its instruments, concepts and subdisciplines

But in my opinion an alternative explanation of the changes that have occurred since the end of World War II until the end of the twentieth century, the late-modern chemistry could be grouped around two revolutions. The fourth chemical revolution<sup>21</sup> is not characterized by the resolution of a dispute, as was the case in the previous three, but on significant changes in the emphasis of research and scientific practice<sup>22</sup> and in the structure of academic and professional organizations. From that moment physics and biology held a prominent place in the interest (biochemistry) and thinking (quantum physics) of chemists.<sup>23</sup>

In summary, we should remember that history deals with two opposite positions: continuity and rupture. In Table 2 different points of view on this issue and related to chemistry are shown.

#### The fifth chemical revolution: 1973–1999

The scientific enterprise is now largely involved in the creation of novelty -in the design of objects that never existed before and in the creation of conceptual frameworks to understand the complexity and novelty that can emerge from the known foundations and ontologies.

<sup>&</sup>lt;sup>21</sup> Identified as the second revolution by Morris (2002a).

<sup>&</sup>lt;sup>22</sup> For example: The chemistry laboratory changed more between 1950 and 2000 than from 1600 until 1950 (Lazlo 2006).

<sup>&</sup>lt;sup>23</sup> An initial discussion of this revolution was done in the Lovain 2013' ISPC Summer Symposium.

Ruptures	Characteristics	Authors
None	Nor scientific neither chemical	Shapin (1996)
One	Lavoisier discarded phlogiston [Chemical revolution, 1784]	Kuhn (1970) McEvoy (2010)
Two	[Chemical Revolution, 1784] [Quiet revolution, 1850–organic chemistry]	Rocke (1993)
	[Classical chemistry, 1700–1940] [Modern chemistry, 1940–today]	Klein (2012)
	[Chemical revolution, 1780] [Instrumental revolution, 1945–today]	Morris (2002b)
Three	[Chemical revolution, 1770–1790] [Quiet revolution, 1855–1875] [Third chemical revolution, 1904–1924]	Jensen (1998)
	Considering instruments [Chemical revolution, 1766–1808] [Quiet revolution, 1830–1860] [Third chemical revolution, 1897–1923]	Chamizo (2014)
Five	Considering instruments and subdisciplines [Chemical revolution, 1766–1808] [Organic chemistry revolution, 1837–1860] [Physical chemistry revolution, 1897–1923] [Instrumental revolution, 1945–1965] [Organometallic, green, supramolecular, nano, femto, 1973–1999]	Chamizo (2011, 2016)

 Table 2
 Ruptures in the history of chemistry

Each chemical revolution in brackets

And precisely because we create those objects and representations we must assume moral responsibility for them. Schweber (1993)

It is a complex and difficult decision to choose between so many new developments in chemistry. Despite those identified in Table 1 other subdisciplines appeared as sonochemistry that even with many books and book series do not change fundamentally what we understand by chemistry.<sup>24</sup> The same can be said of concepts. During the nearly three decades of this period they have appeared and/or consolidated numerous and important concepts, several of them associated with the research done by Nobel laureates in chemistry such as: boranes; dissipative structures; chemiosmotic-theory; HOMO–LUMO; solid matrix.<sup>25</sup> All of them, and certainly other more, were of particular importance but somehow still in the tradition of the "normal chemistry" developed above. However, the coincidence in the emergence and consolidation of new instruments,<sup>26</sup> concepts and sub-disciplines allows recognizing the period from 1973 to 1999 as a deep transformation in the very heart of chemistry.<sup>27</sup> That is to say, the size and type of objects (substances), the way

<sup>&</sup>lt;sup>24</sup> See, for example: Suslick (1988), Price (1992) and Mason (1990, 1991, 1993, 1996, 1999, 2001).

<sup>&</sup>lt;sup>25</sup> See for example the Nobel Lectures: Lipscomb (1976), Prigonine (1977), Mitchell (1978), Fukui and Hoffmann (1981) and Merrifield (1984). http://www.nobelprize.org/nobel\_prizes/chemistry/laureates/: consulted 13/08/2016.

<sup>&</sup>lt;sup>26</sup> Besides the major improvement of old ones.

<sup>&</sup>lt;sup>27</sup> Recently Cerruti (2016) identified a similar period (1975–1995) "Towards complexity chemistry" (Verso la chimica della complessità).

in which they must be done and the time in which they are transformed. In one way or another, chemistry' limits had been set out.

Two slightly separate events serve to mark the beginning of the fifth chemical revolution: the awarding of the Nobel Prize for Chemistry in November of 1973,<sup>28</sup> to organometallic chemistry and *Nature*'s paper in the summer of 1974, about the reduction of the ozone layer in the earth's atmosphere. The fourth revolution and its subsequent short period of normal science were the seed of the fifth revolution, allowing to "see" the world, which could had not been seen before. Broader, more complex, technoscientifically with less boundaries, the fifth revolution, like the previous one, is characterized by significant changes in the emphasis of scientific research and practice, as well as in the structure of academic and professional organizations. Three new instruments allowed arriving to the frontiers of chemistry. Many new sub disciplines appeared.

In 1973 the Nobel Prize in Chemistry was awarded to Ernst Otto Fischer and Geoffrey Wilkinson "for their pioneering work, performed independently, on the chemistry of the organometallic, so called sandwich compounds". Although by that time, the chemical community had already experience in investigating compounds with metal-carbon bond, based mainly on Edward Frankland's research in the nineteenth century and then with Victor Grignard's organomagnesium compounds at the beginning of twentieth century, and later by the studies of the anti-knock gasoline (with tetraethyl lead) and catalysts (Reppe, Ziegler and Natta, Wilkinson), the ground of organometallic chemistry was not fully consolidated. Since then this marginal branch of chemical knowledge has not stopped its development. Marginal because since the early nineteenth century until the end of the twentieth century Jons J. Berzelius established the internal borders of chemistry as organic and inorganic.<sup>29</sup> Organometallic chemistry with some of its new concepts such as "hapticity", "metal cluster compounds" or "fluxionality" was incorporated in the curricula of degrees in chemistry almost anywhere. Specific textbooks were written or translated in different countries,<sup>30</sup> laboratory practices were designed and new specialized magazines were founded.<sup>31</sup>

Instruments developed during the period of normal science between the fourth and fifth revolution and refined in the 1970s and the 1980s helped significantly to the development of organometallic chemistry. Besides <sup>1</sup>H Nuclear Magnetic Resonance introduced and used in the Fourth Chemical Revolution,<sup>32 13</sup>C Nuclear Magnetic Resonance become almost essential in organometallic labs around the world. Related to the role played by J.D.

<sup>&</sup>lt;sup>28</sup> This year also Hans Dehelmet and coworkers isolated and precisely characterized one isolated electron in a trap (Wineland et al. 1973)...electrons become real stuff! Wineland was awarded with the Physics Nobel Prize in 2012.

<sup>&</sup>lt;sup>29</sup> For example "The Third Chemistry" was the name of a book about organometallic chemistry appeared in those years (Ojlobistin 1971).

<sup>&</sup>lt;sup>30</sup> For example: Coates and Green (1975), Collman and Hegedus (1980), Lukerhart (1985) and Elschenbroich and Salzer (1992).

<sup>&</sup>lt;sup>31</sup> For example in 1982 appeared *Polyhedron* and *Organometallics*, one of the ten most cited chemistry journals.

<sup>&</sup>lt;sup>32</sup> As Reinhardt indicated (2006a, p. 223): The boost in the use rate of NMR in organic chemistry during 1961 and 1962 points to a crucial precondition: the availability of a suitable, and affordable, NMR spectrometer. In 1961 the first routine NMR spectrometer, the Varian Associates A-60, appeared on the market. This new instrument enabled organic chemists who were not specialists in NMR to obtain meaningful data by themselves, without help from experts. Between 1960 and 1964, 101 American university chemistry departments reported that they acquired eighty A-60 spectrometers, plus twenty-five NMR spectrometers of a more advanced type. Thus, the wide dissemination of instrumentation went hand in hand with the breakthrough of NMR.

Roberts one of the most important chemists at CalTech, in the development of this last instrument, the historian of chemistry Reinhardt (2006b, p. 238) indicated:

The standard view rates scientific performance in terms of numbers of citations, amounts of funding, and prestige of prizes. Instruments could help to achieve these scientist' goals, when connected to establish research traditions. Lead users of instruments in science came to be, together with the manufacturers, the connectors of high-tech instrumentation and chemical research programs. In doing so, they became first movers and innovative players in a scientific market of citations, grants, and accolades. A lead user paved the way for other scientists, and he did so most efficiently while pursuing and taking advantage of the development and popularization of instruments and methods.

Thus, although multinuclear NMR began to develop during the period of normal science between the Fourth and Fifth Chemical Revolutions, it is mainly during the latter that a level of perfection in sensitivity and resolution was reached, thanks to the work of Richard E. Ernst, winner of the Nobel Prize in Chemistry in 1991. His contribution made multinuclear FT NMR mandatory in almost any chemistry research laboratory around the world. As it can be read in the 1991 Nobel Foundation Press Release, published as "Revolutionary developments make a spectroscopic technique indispensable for chemistry":

The 1991 Nobel Prize in Chemistry has been awarded to Professor Richard R. Ernst of the ETH, Zurich, for important methodological developments within nuclear magnetic resonance (NMR) spectroscopy. NMR spectroscopy has during the last twenty years developed into perhaps the most important instrumental measuring technique within chemistry. This has occurred because of a dramatic increase in both the sensitivity and the resolution of the instruments, two areas in which Ernst has contributed more than anybody else... This discovery is the basis of modern NMR spectroscopy. The ten-fold, and sometimes hundred-fold, increase in sensitivity has made it possible to study small amounts of material as well as chemically interesting isotopes of low natural occurrence, e.g. carbon-13. The enormous potential of the new technique—called FT NMR—quickly became obvious to NMR spectroscopists. The chemical research community got access to it in the early seventies through commercial FT NMR instruments. Nowadays, practically no other types of NMR spectrometer are manufactured.<sup>33</sup>

In 1974 Sherwood Rowland and Mario Molina published the results of their research on the effect of chlorofluoroalkanes in the ozone layer. It was not the first time that chemical companies and governments around the world faced difficulties for its ability to pollute the

<sup>&</sup>lt;sup>33</sup> A similar, but not so spectacular, situation in the refinement of an instrument is found in X-ray spectroscopy throughout the Fifth Chemical Revolution. X-ray tubes, with successive improvements, were used as the primary X-ray source for crystallography experiments from the introduction of this instrument in chemistry to the 1970s, when X-ray synchrotron radiation began to be used. Synchrotrons dedicated exclusively to X-ray production appeared in the 1980s, and since then their numbers have been increasing. As the instrument-developer Arndt said (2001, p. 465): *In 1971, K.C. Holmes FRS and his co-workers first demonstrated the usefulness of synchrotron radiation at Hamburg for recording the feeble diffraction pattern from insect flight muscle. Today synchrotron radiation from X-rays beam lines at some hundreds of electron storage rings on three continents provide beam intensities up to 1000 times greater than those from the most powerful X-ray tubes. In addition to providing ever-higher and higher intensities, synchrotron sources have the advantage over X-ray tubes that allow the easy selection of the most suitable X-ray wavelength for a particular investigation.* 

environment but this time, unlike all previous, the damage and the risk were unequivocally global. In this sense a couple of years earlier the use of DDT in the United States was banned. In 1995 Paul J. Crutzen, Mario J. Molina and F. Sherwood Rowland awarded Chemistry's Nobel Prize "for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone". As Rowland said:

The starting point for that work was the discovery by Jim Lovelock that the molecule, CCl<sub>3</sub>F, a substance for which no natural sources have been found, was present in the Earth's atmosphere in quantities roughly comparable to the total amount manufactured up to that date. Lovelock had earlier invented an extremely sensitive detection system employing electron capture (EC) by trace impurities, and attached it to the column of effluent gases from a gas chromatograph (GC), a device which separates a mixture of gases into its individual components. With this ECGC apparatus, Lovelock initially established that CCISF was always detectable in the atmosphere near his home in western Ireland, and then that it was also present in all of the air samples tested on the voyage of the R.V. Shackleton from England to Antarctica (Rowland 1995).

The Electron Capture Detector (ECD) was invented and refined in the late 1950s by Lovelock (1974) during their stay in the National Institute for Medical Research where he was a colleague of A. Martin (Nobel Prize in Chemistry in 1952) and T. James, inventors of gas–liquid chromatography. This instrument was fundamental in monitoring DDT during the 1960s and fluorocarbons in the 1970s.

In an ECD<sup>34</sup> (a closed chamber of less than 2 ml of volume) a source of radiation (initially pieces of silver foil containing <sup>90</sup>Sr, but actually <sup>63</sup>Ni) is used to bombard the carrier gas (usually nitrogen or argon) which passes through an ionization chamber, thus generating a plasma of positive ions, free radicals and electrons. The latter are picked up in a collector electrode, and thus can establish a stable baseline current in the presence of pure carrier gas. When a halogenated substance penetrates together with the carrier gas can capture electrons, generating negative ions of lower mobility than the electrons themselves or neutral fragments by recombination with the positive ions of the plasma generated in the original process. A drop in the potential detects the fall in the number of electrons across the walls of the ECD, which can be related quantitatively to the amount of the halogenated substance that is going through the detector.<sup>35</sup> The final version of the ECD was highly sensitive, but only for halogenated compounds with a strong affinity for electrons. Initially, experiments with this instrument showed that a tiny amount of carbon tetrachloride on the silicone seal, for instance, was sufficient to sabotage any subsequent attempts to use it. As Lovelock pointed out (Lovelock 2002, p. 186):

<sup>&</sup>lt;sup>34</sup> Lovelock recalled making his first prototype and, characteristically, he emphasised its home-made character (Lovelock 1998, p. 6): *My first detector was a simple cylindrical ion chamber, about two millilitres in volume and contained a one billion Becquerel strontium 90 source of beta radiation. I remember bending the stiff and fiercely radioactive foil behind a sheet of thick glass until it fitted the detector cavity...In the middle of the cavity was a small collecting electrode, connected to a home-made electrometer. The chamber was polarised by connecting the outer case to a voltage source...and was used an automobile spark-plug as the insulator that held the anode. The electrometer was quite literally home-made—it used a pair of vacuum tubes in a balanced cathode follower circuit and I made it on our kitchen table.* 

<sup>&</sup>lt;sup>35</sup> The ECD is the nose that smelled the onset of environmental corruption. It discovered the global distribution of the CFCs, the pesticides, and the PCBs, and it is still used to monitor their abundance. New uses of the ECD include the detection of perfluorocarbons used as tracers to measure air and water mass movements (Bud and Warner 1998, p. 214).

It was then, and stills is, the most sensitive easily portable and inexpensive analytical device in existence. It is not easy to describe the exquisite sensitivity of the ECD. One way is to imagine that you had a wine bottle full of a rare perfluorocarbon liquid somewhere in Japan and that you poured this liquid onto a blanket and left it to dry in the air by itself. With a little effort, we could detect the vapour that had evaporated into the air from the blanket here in Devon a few weeks later. Within two years, it would be detectable by the ECD anywhere in the world.

Lovelock has spent his career as an independent scientist defying the mainstream thought. He is famous for his Gaia hypothesis, which suggests the Earth as a self-regulating system that enables life to exist on the planet.<sup>36</sup>

After a strong struggle with the chlorofluoroalkanes' chemical industry, where Molina and Rowland played an active role, the political response to ozone layer depletion was the Montreal Protocol.<sup>37</sup> Signed in the eighties by more than 200 countries, it is the first universally ratified treaty in United Nations history. So after the publication of Rachel Carson's *Silent Spring* in the sixties, the foundation of the US Environmental Protection Agency in the seventies, green chemistry<sup>38</sup> with its 12 principles<sup>39</sup> was born (Clark 2006;

<sup>37</sup> The Montreal Protocol on Substances that Deplete the Ozone Layer was designed to reduce the production and consumption of ozone depleting substances in order to reduce their abundance in the atmosphere, and thereby protect the earth's fragile ozone layer. The Montreal Protocol includes a unique adjustment provision that enables the Parties to the Protocol to respond quickly to new scientific information and agree to accelerate the reductions required on chemicals already covered by the Protocol. These adjustments are then automatically applicable to all countries that ratified the Protocol... The Parties to the Montreal Protocol have amended the Protocol to enable, among other things, the control of new chemicals and the creation of a financial mechanism to enable developing countries to comply... (Ozone Secretariat 2016).

<sup>38</sup> Few arguments about its novelty in this journal are: As a matter of fact, green chemistry seems to correspond to a radical change in the history of chemistry, and not merely to a green washing exercise undertaken by chemist in order to improve the public image of their scientific and industrial domain (Llored and Sarrade 2016 published on line); green chemistry is a new practice of chemistry suitable to bring Sustainability into chemical products and process (Marques and Machado 2014, p. 127); green chemistry is not different from traditional chemistry in as much as it embraces the same creativity and innovation that has always been central to classical chemistry. However, there lies a difference in that historically synthetic chemists have not been seen to rank the environment very high in their priorities. But with an increase in environmental consciousness throughout the world, there is a challenge for chemists to develop new products, processes and services that achieve necessary social, economical and environmental objectives (Kidwai and Mohan 2005, p. 271).

<sup>39</sup> The twelve principles are: (1) It is better to prevent waste than to treat or clean up waste after it is formed. (2) Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product. (3) Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment. (4) Chemical products should be designed to preserve efficacy of function while reducing toxicity. (5) The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used. (6) Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure. (7) A raw material of feedstock should be renewable rather than depleting wherever technically and economically practicable. (8) Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible. (9) Catalytic

<sup>&</sup>lt;sup>36</sup> As he said: In 1961 I received a letter from the director of space flight operations of NASA that was to change my life. I was invited to be an experimenter on the forthcoming Surveyor missions to the Moon whose object was to analyze and examine the lunar regolith ahead of the landing of the astronauts. How could anyone whose life plan was to reduce scifi to practice refuse such an offer? It led to the fulfilling and rich field of science opened up by the view of the Earth and the planets from above. It led me to what I like to think is the most significant invention of my life, namely, the theory of the Earth as a self-regulating system—what I like to call Gaia (Lovelock 1995, p. 249).

Linthorst 2010). This evolved new concepts like "atom economy", "life cycle analysis", or also in its chemical context "sustainable<sup>40</sup>" as books, journals, courses, conferences and institutes around the world can testify.<sup>41</sup> About this Roald Hoffmann, awarded with the Nobel Prize in chemistry in 1981 said:

The ecological imperative has crept down much more slowly to inventive yet unconcerned academia. However, I see its formative events there—in the interest in atmospheric chemistry and the ingenious construction of novel organic processes to avoid the use of organic solvents. A government carrot in the form of new research funds for green chemistry would, in my unpopular opinion, be just what is needed to channel the ingenuity of my colleagues, who love to say that they just want to de what is interesting, but...The same nicely obsessive penchant for control as that which is used to make molecules do acrobatics can and is being turned to the attainment of a necessary balance between our given imperative to create and our love for the world (Hoffmann 2000, p. xi).

The fifth revolution marks the time when the community learned to make chemical reactions in less extreme conditions (in terms of pressure, temperature and solvents) than hitherto used. They were approaching conditions that allow life and decrease the generation of potential contaminants. When chemistry becomes biology, molecular interactions are less intense, and molecular aggregates can be recognized in the so called supramolecular chemistry. Thus the 1987 Nobel Prize in Chemistry was jointly awarded to Donald J. Cram, Jean-Marie Lehn and Charles J. Pedersen "for the development and use of molecules with specific structural interactions of high selectivity". Lehn defined supramolecular chemistry as chemistry beyond the molecule containing more organized complex entities, resulting from the association of two or more chemical species through intermolecular forces. In his own words (2000, pp. 303–304):

In 1935 Klaus Wolf introduced the term Übermoleküle to describe molecular associations, such as the acetic acid dimer, that were clearly not covalently bound. Yet it was not until 1980s that these elements emerged into a coherent framework of supramolecular chemistry. Why this delay?

One reason is concrete enough: only in the past few decades have the powerful physical methods that are needed to analyse the structures and properties of supramolecular assemblies existed. Spectroscopies, particularly nuclear magnetic resonance, have been refined to a degree that allows the structure and dynamics of

Footnote 39 continued

reagents (as selective as possible) are superior to stoichiometric reagents. (10) Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products. (11) Analytical methodologies need to be further developed to allow for real-time, in process monitoring and control prior to the formation of hazardous substances. (12) Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

<sup>&</sup>lt;sup>40</sup> Sustainable and green chemistry in very simple terms is just a different way of thinking about how chemistry and chemical engineering can be done. Over the years different principles have been proposed that can be used when thinking about the design, development and implementation of chemical products and processes. These principles enable scientists and engineers to protect and benefit the economy, people and the planet by finding creative and innovative ways to reduce waste, conserve energy, and discover replacements for hazardous substances (ACS 2016).

<sup>&</sup>lt;sup>41</sup> See for example: Anastas and Williamson (1996), Anastas and Warner (1998), Collins (1995), Clark (1999), Lancaster (2002) and Matlack (2001).

these systems to be studied in great detail in solution, while X-ray diffraction techniques can now routinely reveal their complex crystal structure. Equally important for a field to ripen and mature is a receptive and fertile scientific scene— one that is able and prepared to embrace ideas from diverse disciplines and to recognize connections between them; and that has the vision to set new agendas and objectives without any guarantee that they will be attained or that they will in the end have justified the effort.

Besides the spatial arrangement, and the architecture of their components Lehn also characterized supramolecular chemistry as "soft chemistry" because is concerned with soft bonds. As in the other subdisciplines that characterized the fifth revolution, new journals and books<sup>42</sup> about supramolecular chemistry were published. Among all the instruments used in this sub-discipline multinuclear FT NMR was the most important.<sup>43</sup> Also a wide and new vocabulary, like crown ethers, cryptands, catenanes, host–guest compounds, self-assembly or self-organization,<sup>44</sup> was coined.

Closely related to supramolecular chemistry is nanochemistry. Nanochemistry refers to the possibility of using chemical synthesis knowledge to build molecular aggregates of size, shape, composition or specific surface.<sup>45</sup> With multiple applications today, from medicine, cosmetics or materials, the origin of nanochemistry can be placed with the discovery of fullerenes in 1984 by Robert Curl, Harold Kroto and Richard W. E. Smalley, and subsequent synthesis of carbon nanotubes. They won the 1996 Nobel Prize in Chemistry. Ten years earlier, in 1986, Gerd Binnig and Heinrich Rohrer awarded the Physics Nobel Prize "for their design of the scanning tunnelling microscope (STM)", instrument which allows to "see"<sup>46</sup> atoms and, in one of its modifications, the Atomic Force Microscope, assembles them.

<sup>&</sup>lt;sup>42</sup> Specific journals like *Supramolecular Chemistry* starts in 1992, and some years latter *Journal of Supramolecular Chemistry*; many books with this name appeared but Lehn (1995) and Steed and Atwood (2000) are some of the more relevant.

<sup>&</sup>lt;sup>43</sup> As Pons indicated in his book' introduction (1999): NMR is better suited than any other experimental technique for the characterization of supramolecular systems in solution.

<sup>&</sup>lt;sup>44</sup> The last two terms have been used in a interchangeably way, so are defined properly as (Lehn and Ball 2000, p. 304):

Self assembly is the spontaneous association of several (more than two) molecular components into a discrete, non-covalently bound aggregate with a well-defined structure. This will generally involve more than one kinetically distinct step. Self assembly involves molecular-recognition process—binding events, but not 'mere' binding. Rather, one may say that recognition is binding with a purpose.

Self-organization is the spontaneous ordering of molecular or supramolecular units into a higher-order noncovalent structure characterized by some degree of spatial and/or temporal order or design—by correlations between remote regions. A self-organized system may be either at equilibrium or in a dynamic state characterized by several stable configurations; and it will exhibit collective (and often non-linear) behaviour. Such a definition does not (and need not) exclude crystallization and related ordering phenomena such as liquid-crystallinity.

<sup>&</sup>lt;sup>45</sup> If nanoscience is concerned with making, manipulating and imaging materials having at least one spatial dimension in the size range of 1–1000 nm and nanotechnology can be defined as a device or machine, product or process, based upon individual or multiple integrated nanoscale components, then what is nanochemistry? In its broadest terms, the defining feature on nanochemistry is the utilization of syntethic chemistry to make nanoscale building blocks of different size and shape, composition and surface structure, charge and functionality (Ozin et al. 2009, p. 13).

<sup>&</sup>lt;sup>46</sup> The images produced by the STM are still not pictures in the conventional sense, because they depend on electrical currents, not light, and therefore represent a new way of seeing (Von Bayer 1994, p. 68).

The STM was invented at IBM laboratories in Zurich. The problem them was the detection of defects in the oxide films junctions used in high-speed computers.<sup>47</sup> Henri Rohrer and his Ph.D. student Gerd Binnig were successful in locate pinholes by probing the electrical characteristics of the films developing the STM. Using an analogy, it is possible to compare STM to Braille reading. In this instrument, a thinnest metal tip (usually made of tungsten or platinum-iridium)<sup>48</sup> approaches the surface of a material surface (at least slightly electrically conductive) to a distance of about 1 angstrom, so that if a small potential difference is applied due to the tunnel effect,  $^{49}$  a weak electrical current (~1 nA) is established. The current is very sensitive to the distance between the tip and the material. When the tip is swept across the surface, the tunnelling current can be precisely detected.<sup>50</sup> Hence through the appropriate electronic devices, a topographical image of the sample surface is obtained (Griffith and Kochanski 1990).<sup>51</sup> Using this instrument different surfaces of various materials in addition to molecules adsorbed in them have been studied with research purposes as well as recently education purposes.<sup>52</sup> Furthermore manipulation and modification by adjusting the tip-sample distance, or by changing the bias voltage across the junction allow taking one by one atoms and draw different images with them (Crommie et al. 1993).

Together with Ernst Ruska,<sup>53</sup> Gerd Binning and Heini Roher awarded the 1986 Physics Nobel Prize. In his Award Ceremony Speech Professor Johansson said (1986):

The microscope can be regarded as an extension of the human eye. But sight is not the only sense we use to orientate us in our surroundings, another is feeling. With modern technology it is possible to construct equipment that is based on the principle

<sup>49</sup> Tunneling is described as: According to quantum mechanics a subatomic particle can pass through a spatial region in which the particle's kinetic energy is less than its potential energy...The observation of the tunneling effect in a variety of systems has offered direct evidence of quantum mechanics in action. Some of the landmarks are: field emission from metal, ionization of hydrogen atoms...alpha particle decay process in heavy atoms...and STM (Meyers 2000, p. 9285).

 $^{50}$  STM requires to works properly Ultra High Vacuum (UHV),  $<10^{-8}$  mbar and to achieve atomic resolution, vibration isolation is essential.

<sup>&</sup>lt;sup>47</sup> *IBM*, along with the raft of other high tech companies that are pursuing nanotechnology, no doubt seeks truth, but not at the expense of shareholders...nanotechnology, including the instruments that make it possible, such as the scanning tunnelling microscope, is developing in a much more thoroughly integrated academic/commercial matrix (Baird and Shew 2004, p. 146).

<sup>&</sup>lt;sup>48</sup> Making tips remains something of a dark art. One takes a piece of tungsten or platinum-iridium wire and cuts it with wire cutters, being careful to pull away from the end that will serve as the tip. Some researchers develop a good knack at this, while others do not. While tips are usually diagrammed as nice symmetrical ice-cream cone structures, in reality they are messy affairs resembling a jagged mountain range. But was is crucial is that one peak from this range be sufficiently higher than all the others and itself be atomically sharp; it then can serve as the point through which the tunnelling current passes (Baird and Shew 2004, p. 147).

<sup>&</sup>lt;sup>51</sup> Two commentaries of von Bayer (1994) are useful: *Contrary to appearances (the STM image) it was not an actual photograph but a computer reconstruction based on measurements of the electric current that flowed through the tip of a needle as it passed across the molecule' surface. A hidden chain of readings, calculations and interpretations stood between the sample and the final image* (p. 63). *The use of color in atomic images, false through it is, has a profound impact: it restores to atoms an element of the reality that they has lost. Besides shape, texture, weight, and hardness, real objects have color, no matter how drab it may be...the scientist who produce STM images color them for reasons other than emotional appeal or the hope of making them more real. A simple purpose of color coding is the identification of different species of atoms* (p. 80).

<sup>&</sup>lt;sup>52</sup> See for example: Wiesendanger and Güntherodt (1993), Von Bayer (1994), Chiang (1997), Li-Jun (2006), Chen (2008) and Ewers et al. (2014).

<sup>&</sup>lt;sup>53</sup> He was awarded "for his fundamental work in electron optics, and for the design of the first electron microscope".

of feeling, using, for example, a sort of mechanical linger. The "finger" may be a very fine needle which is moved across the surface of the structure to be investigated. ... A crystal surface which appears completely flat in a microscope is seen with this instrument to be a plain on which atoms rise like hills in a regular pattern...This is just the beginning of an extremely promising and fascinating development. The old dream from antiquity of a visible image of the atomic structure of matter is beginning to look like a realistic possibility, thanks to progress in modern microscopy.

The Atomic Force Microscope (AFM), invented by Binnig in 1986 is the direct extension of the scanning tunneling microscope especially useful in the study of surfaces of non-conductive materials. This instrument, instead of detecting the tunnel current between tip and sample, controls the force (about 0.01  $\mu$ N) experienced between the atoms on the tip-end (actually made from Si or silicon nitride) and the atoms of the surface of the material (insulator or conductive). With this instrument a DNA segment can be cut and picked up (An et al. 2007).

The end of the fifth revolution can be identified when Ahmed Zewail was awarded with the 1999s Nobel Prize in Chemistry "for his studies of the transition states of chemical reactions using femtosecond spectroscopy".

In chemistry a re-arrangement occurs when the atoms in a molecule change their specific order. At that instant, the precise moment of the activated complex, old bonds disappear and new ones are formed. At this precise moment dissociation energies are being redistributed among them. The time scale in chemistry is, therefore, the time scale of the motion of atoms (Remacle and Levine 2008). Although there are chemical phenomena that last for billions of years, the most basic processes take place at few femtoseconds  $(1 \times 10^{-15} \text{ s})$ . I share the idea that chemical processes, in other words molecular reaction dynamics, are the core of our discipline,<sup>54</sup> not to say that the conceptual apparatus to describe them is surprisingly poor compared with that to describe structures (Weininger 2000). As Manz and Wötse indicated (1995, p. v):

When in 1949 George Porter performed the first millisecond flash photolysis experiments he initiated a 'race against time'. Over the past 40 years, temporal resolution in the observation of chemical processes has increased by eleven orders of magnitude! The development reached the ultimate femtosecond resolution in Ahmed Zewail's direct observation of chemical reactions as they produced along the reaction path, from reactants via the transition state toward the products. This, 1987 breakthrough, which was the culmination of his efforts over a decade, marks the birth of a new scientific field at the interphase between experiment and theory, chemistry and physics, with numerous applications covering all phases of matter...Femtosecond Chemistry.

In a flash photolysis experiment<sup>55</sup> the original molecules in a vacuum chamber were excited with a flash beam. In the original Porter's experiments the beam was a white light

<sup>&</sup>lt;sup>54</sup> In an Editorial of Hyle its editor Schummer (2004) said: the general important point I want to make, and my reason to devote an entire editorial to this, is that there are fundamental questions waiting to be addressed by philosophers of chemistry, philosophical questions that require both chemical understanding and philosophical knowledge and skills, and not just a familiarity with the technicalities of some theory or with the writings of one particular philosopher. Whether chemistry is primarily about things or about processes does not follow from any experiment or theory but is, knowingly or not, rather presupposed instead, and such is the nature of a philosophical question.

<sup>&</sup>lt;sup>55</sup> The study of chemical events that occur in the femtosecond timescale is the ultimate achievement in half a century of techniques for the study of fast reactions and, although many future events will be run over the same course, chemist are near the end of the race against time, Porter (1995, p. 3). George Porter was awarded in 1967 with the Nobel Prize in Chemistry.

flash, meanwhile in Zewail's experiments a Ti–sapphire laser produced the beam.<sup>56</sup> This new instrument, (the Ti–sapphire laser which pulses as short as 4 fs) with all the other optical equipment and the laser-induced fluorescence detector becomes a single integrated instrument to measure the time required to break and form chemical bonds. The laser beam<sup>57</sup> injects two pulses. With the first one the molecule breaks into products. The second pulse allows monitoring the original molecule. Controlling the time interval between the two pulses, it is possible to recognize how quickly the original molecule changes. An important development in this kind of experiment was the introduction of the split-beam pulse. That means that one part of the beam goes through the reaction mixture and causes photolysis; the other one by-passes the reaction mixture, goes to a movable mirror and its reflected back to the reaction mixture through a fluorescent lamp solution which converts the beam into continuous radiation in the visible. This is then detected and analysed.<sup>58</sup>

After using a flash photolysis with Ti-sapphire laser beam integrated instrument, Zewail said:

The concept of the atom, proposed 24 centuries ago and rejected by Aristotle, was born on a purely philosophical basis, surely without anticipating some of the 20th century's most triumphant scientific discoveries. Atoms can now be seen, observed in motion, and manipulated. These discoveries have brought the microscopic world and its language into a new age, and they cover domains of length, time, and number. The length (spatial) resolution, down to the scale of atomic distance (angstrom,  $1 \text{ Å} = 10^{-8} \text{ cm}$ ), and the time resolution, down to the scale of atomic motion (femtosecond,  $1 \text{ fs} = 10^{-15} \text{ s}$ ), have been achieved (Zewail 2001).

### Conclusions

The major purposes of chemical education in the 21st century will be to introduce all young people to the implications of chemical technologies and to provide the basis for the advanced study of chemistry by only some of those young people. In order to address both these purposes adequately, the future curriculum at all levels will have to reflect, to a far greater degree than is currently the case,

<sup>&</sup>lt;sup>56</sup> Instrument first constructed in 1982. Here is important to remember J.C. Maxwell quotation: *Instruments are those that were specifically made for scientific experiments* (cited in Bud and Warner 1998, p. ix).

<sup>&</sup>lt;sup>57</sup> As Zewail indicated: Flashing a molecule with a femtosecond laser pulse can be compared to the effect of a stroboscope flash or the opening of a camera shutter. Thus a pulse from a femtosecond laser, combined with an appropriate detector, can produce a well-resolved "image" of a molecule as it passes through a specific configuration in a process of nuclear rearrangement (2001, p. 740).

<sup>&</sup>lt;sup>58</sup> A physical chemistry textbook explanation of a specific experiment indicated: Until very recently there were no direct spectroscopic observations on activated complex, for they have a very fleeting existence and often survive for only a few picoseconds. In a typical experiment designed to detect an activated complex, a femtosecond laser pulse is used to excite a molecule to a dissociative state, and then a second femtosecond pulse is set at absorption of one of the free fragmentation products, so its absorption is a measure of the abundance of the dissociation product. For example when ICN is dissociated by the first pulse, the emergence of CN from the photoactivated state can be monitored by watching the growth of the free CN absorption. In this way it has been found that the CN signal remains zero until the fragments have been separated by about 600 pm, which takes about 20 fs (Atkins and de Paula 2006, p. 892).

*trends in chemistry itself.* Gilbert (2006)

In the last 50 years many attempts have been done to change the practice of traditional school "general" chemistry.<sup>59</sup> Despite these major efforts, the results were rather disappointing<sup>60</sup> and Schwab's (1962) interpretation of science taught as a dogma or as "a rhetoric of conclusions" remains. Furthermore, little by little, we recognize that our classroom practice is deeply embedded within philosophical approaches.<sup>61</sup>

Despite the tradition that the research about nature of science<sup>62</sup> already has, many chemistry textbooks suggest erroneously that scientific results come from the mind of a great scientist. However, neither the way these achievements were done nor the attitudes and the instruments that were needed are really discussed. Since processes are ignored, there is no room to develop professional skills such as setting up experiments, evaluating experimental results, and discussing alternative interpretations or models. Professional attitudes, like open-mindedness, willingness to suspend judgment, objectivity, and so on, also stay out of the picture. Apart from this Schummer (2006) and Talanquer (2013) suggest that chemistry is a transgressive science that resists the dogmatic classifications often founded in studies of nature of science. Chemists do not observe nature passively as they measure to achieve transformations (Hoffmann 2007) through the chemical experiment (Chamizo 2013b).

Despite the fact that this approach to the five scientific revolutions and exemplars, instruments, sub-disciplines and lexicons can be subject of many unsolved controversies, leaves out many technical details, as well as protagonists and the broader social context, all of them essential for the proper understanding of how chemistry developed, could help to teach chemistry from an historical approach. The fifth chemical revolution gives the possibility to think about realism and antirealism, a forgotten subject in chemistry class-rooms.<sup>63</sup> Electrons, atoms and molecules became realities that can be isolated, "seen" and manipulated ...at the limit of time...not without controversies. As Lehn said:

Some believe that nanotechnology will arise from the manipulation of individual atoms—that molecular—scale devices will be built by putting their constituent atoms into position one by one. That has undoubtedly become a real possibility in the four decades since the physicist Richard Feynman asked the prophetic question 'What would happen if we could arrange atoms one by one the way we want them? The development of STM in the 1980s provided a tool not just for seeing atoms but also for moving them about. When in 1991 Don Eigler and colleagues at IBM's Almaden Research Center in San José wrote their company's name in 35 xenon atoms on

<sup>&</sup>lt;sup>59</sup> Following the Sputnik's launching several approaches, from *Nuffield Chemistry* and *Chem Study* to *Salters' Chemistry* and *ChemCom*, have been developed and spread to many other countries.

<sup>&</sup>lt;sup>60</sup> See for example: Novak (1977), Fensham (1992), Matthews (1994), Aikenhead (1997), Duschl and Osborne (2002) and Van Aalsvoort (2004).

<sup>&</sup>lt;sup>61</sup> See for example: Duschl (1994), Van Berkel et al. (2000), Erduran and Scerri (2002) and Van Aalsvoort (2004) and also the importance of technology in the chemical enterprise (Sjöström 2007; Bensaude-Vincent and Simon 2008; Chamizo 2013b, 2014).

<sup>&</sup>lt;sup>62</sup> See for example: McComas (1998), Lederman (2007), Matthews (2012), Chamizo et al. (2012) and Hodson (2014).

<sup>&</sup>lt;sup>63</sup> About this Hacking said: *Philosophers of science who discuss realism and antirealism have to know a little about the microscopes that inspire such eloquence. Even the light microscope is a marvel of marvels. It does not work in the way that must untutored people suppose. But why should a philosopher care how it works? Because it is one way to find out about the real world (1983, p. 186). See also: Good (1999).* 

nickel by dragging the atoms into position with the tip of the STM, it seemed that nanotechnology had arrived...However, the fundamental building block of nanotechnology will be not the atom but the molecule... More fundamentally, atomic building blocks cannot be pre-programed—each atom must be put in place 'by hand' which is a laborious task. However, molecules can be designed to assemble in high specific ways, in a gentle manner that uses non-covalent interactions and allows the option of annealing to remove defects. Moreover, the rules of chemistry, may work against atomic assembly—there is far more to linking up real atoms than pushing together effigies in a ball—and stick model...Supramolecular chemistry is developing from its origins in recognition processes, through assembly and organization, to a paradigm in which information is stored, retrieved, transferred and processed at the molecular and supramolecular level (Lehn 2000, pp. 347–349).

It is time to reflection. Ethics, boundaries and realities must be discussed in the chemistry classroom.

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