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PERSPECTIVE

Crossdisciplinary fundamental research—the seed for scientific advance and technological innovation†

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As it was earlier in the 1980's, so it is now, fundamental science research is under threat as decisions are made on science funding by people who do not do fundamental research, seem congenitally incapable of understanding what it is and furthermore in the face of countless examples seem blind to how important it has been to the technologies that govern our modern life and will be to the future technologies that we desperately need to develop to survive. In this article some general observations are made on how the fascination for what happens in space and stars was the key trigger that gave birth to Science itself and a particular case is outlined which indicates that this same fascination is still the catalyst of some fundamental breakthroughs today. This article also outlines an archetypal example of the way major breakthroughs are often made by the synergy that comes from cross-disciplinary research in a way which is totally surprising. In this case it started from a curiosity about the quantum mechanical description of molecular dynamics and involved pioneering advances in synthetic organic chemistry which led to the suprising discovery that some exotic carbon molecules were abundant in space and stars. These results initiated an experiment using a new technology that represented a major breakthrough in cluster science. The upshot was totally unpredictable, the birth of a whole new field of Chemistry as well as a paradigm shift in major areas of Nanoscience and Nanotechnology.

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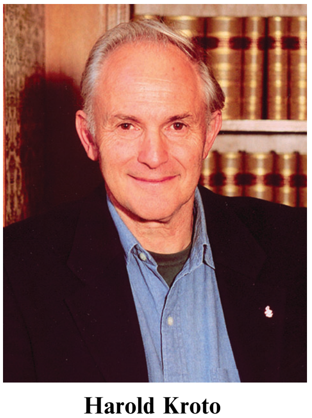

Harold Kroto

Harold Kroto received his BSc and a PhD from the University of Sheffield. He joined the University of Sussex in 1967 and became a professor in 1985 and a Royal Society Research Professor in 1991. In 1996 he was knighted for his contributions to chemistry and, together with Robert Curl and Richard Smalley, received the Nobel Prize for Chemistry for the discovery of C_{60} Buckminsterfullerene. He joined Florida State University in 2004 and is a co-founder of the Vega Science Trust established to promote science education and careers among young people and more recently has initiated the Global Educational Outreach for Science Engineering and Technology (GEOSET) programme.

The age-old awe that man has had for the heavens has had an impact on almost all aspects of human culture and much of our well-understood knowledge. It has furthermore resulted in technologies with overwhelmingly positive and only occasionally negative effect. Arguably the most positive advances have taken place since Galileo recognized that the phases of Venus provided evidence that confirmed the Copernican heliocentric system and cemented his position firmly as the "Father of Science". From this moment on we had, at long last, a straightforward evidence-based philosophical construct which enabled mankind to determine what can be considered "true" with any degree of reliability at all. Prior to this the human race depended more on common sense—knowledge of what works and what doesn't—rather than some sort of deep intellectual understanding of why things worked the way they did. To survive it was not really necessary to know that it was because the Earth was turning on its axis that the Sun appeared to circle the Earth. With this intellectual revolution, which we can call Natural Philosophy, came a powerful new multifaceted language involving symbolic algebra and scientific nomenclature which enabled this knowledge to be efficiently cached in written form and available for general education. Particularly important "truths" have resulted as this new language became available to help us to develop a deeper understanding of the way Universe works. This has led to the birth of astrophysics and development of technologies from

Galileo's telescope to the fantastic satellite-born devices put into space by NASA. These have not only enabled us to observe the planets and stars more clearly but we have been able to see to the very edge of the Universe and make a plethora of discoveries about all its aspects from the matter between stars to the processes that occur deep within them as well as the conditions when the Universe was created. The stimulus to our general technologies over the last 400 years has been extraordinary and we disregard to our peril the importance of fundamental science as the seed of our future technologies.

Arguably the most fundamental of advances in scientific understanding were based on astronomical observations as they led directly to the development of a coherent structure for Classical Mechanics by Newton. In order to understand the motions of the planets and comets he (and Leibniz) developed Calculus, one of our greatest cultural achievements; not just a mathematical one. It was inevitable that, with the development of spectrometers, scientists would start to study the atomic and molecular composition of heavenly bodies such as stars which are hot, often very hot, and comets and the interstellar medium which are very cold. Spectroscopic observations uncovered the existence of an atomic world that Classical Mechanics could not handle and it was in trying to solve these problems that Quantum Mechanics was developed. With the development of radiotelescopes, the interstellar medium was found to be a veritable Pandora's Box, full to the brim with fascinating and exotic molecules as well as mysterious dust particles. In fact we now know that without interstellar molecules, such as carbon monoxide and dust, stars like the Sun and planets like the Earth cannot form, and of course we would not exist.

Particularly fascinating, curious and crucial has been the role that the element carbon has played in almost every aspect of the development of our understanding of both the physical and natural sciences. The fact that the element is at all abundant is due to a curious set of coincidences involving its nucleosynthesis from helium deep inside stars. If one furthermore adds into the overall equation the uniquely profuse chemistry of carbon, *i.e.* Organic Chemistry, it is essentially impossible to conceive that life could be based on any other element. The most recent big surprise that the element had up its sleeve, was the existence of the pure carbon cage molecule C_{60} Buckminsterfullerene, the third well-defined allotropic form of carbon,[1] Fig. 1.

The two extremely well-known and "fairly" well characterised allotropic forms of carbon, diamond and graphite, have been known to mankind since time immemorial. There is a rare diamond-related form called Londsdalite which is sometimes found in minute amounts in objects which have been subjected to unusually energetic physico-chemical processing, such as may occur in meteorite formation. Carbon also turns up in a variety of poorly characterised forms such as for instance the amorphous forms knows as carbon blacks and soots—these often contain high levels of impurities. Another solid form, the mythical creature called "carbyne," has been shown conclusively by Smith and Buseck[2] to be based on erroneous identification of an impurity. It was suggested that this material was crystalline and consisted exclusively of long polyyne chains aligned in bundles. I was convinced, when I first saw this study, that it

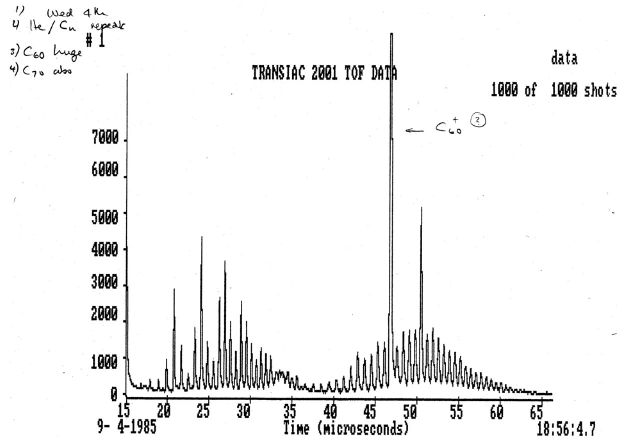

Fig. 1 My print-out of the 4th Sept 1985 time-of-flight mass spectrum of pure carbon clusters, created when a graphite disk is vapourised by a focused laser, that first showed unequivocally that carbon species with 60 and 70 atoms were specially stable.[1] Note my comments in the top left corner and the question mark next to the C_{60} signal which is actually off-scale. The peak exactly at 20 μs belongs to the C_{10}^+ cation. The distribution in the C_n ($n < 30$) low mass range exhibits the previously well-known intensity variation pattern in which C_{11}^+, C_{15}^+, C_{19}^+ and C_{23}^+ are all strong and which it had been suggested quite early on was evidence for monocyclic rings because these particular cations possess numbers of π electrons consistent with the Hückel $4n + 2$ rule *i.e.* 10, 14, 18 and 22. The bimodal distribution shown here had already been pointed out in a 1984 study[3] which suggested that the C_{40}–C_{100} family of even-only carbon species might be "carbynes" (see text).

must be nonsense as it made no chemical sense whatsoever as it is well-known that attempts to condense pure acetylenes invariably results in a major explosion. The original fallacious claim has catalysed and is still catalysing, a significant amount of misguided conjecture[3] by groups unaware of the explosive nature of acetylenes and particularly by astrophysicists who must rely heavily on the reliability of studies by chemistry researchers.

The experiment that uncovered the existence of C_{60}, Buckminsterfullerene[1] has its origins in the conflation of a set of disparate fundamental avenues of study, from a curiosity about the dynamic behavior of long linear chains[4,5] to the synthesis of such chains[4–7] and the suprising discovery that they were unexpectedly abundant in interstellar space.[8–10] Simple curiosity about the origins of the chains in space then resulted in an initially quite unassuming little experiment involving the outstanding technical breakthrough made by Smalley and coworkers in the study of refractory clusters with up to tens of atoms.[11] The unstable small molecular forms of carbon such as C_2 and the interesting triatomic species C_3, characterised in 1951 by Douglas,[12] have been known for decades; they occur in the gas phase and were identified quite a long time ago in flames and discharges as well as in stars and comets. More recently, longer "linear-ish!" chains up to C_9 have been studied in the laboratory and well-characterised by Heath and Saykally.[13,14] Elegant metal catalysed coupling reactions pioneered by Walton[6,7] showed some 40 years ago that long carbon chains with as many as 32 carbon atoms could be synthesised in the laboratory. Walton and coworkers had made these molecules and stabilized them quite by adding bulky end groups. This work can now be recognized as the 1D analogue of the 2D cross-coupling reaction breakthrough which resulted in the Nobel Prize for Chemistry in 2010. Particularly fascinating studies (at least for me) were carried out during the period 1959–64 by Hintenberger and coworkers who produced some intriguing early mass spectrometric data which indicated that species with up to 33 atoms existed in carbon vapour.[15] They and others highlighted a curious mass spectrometric intensity pattern in which the signals for the ions C_{11}^+, C_{15}^+, C_{19}^+ and C_{23}^+ were invariably observed to be stronger than others (Fig. 1). This pattern was interpreted by Pitzer and Clementi[16,17] as evidence for monocyclic ring structures as this is what the Hückel $4n + 2$ aromaticity rule predicted. The cations of C_n^+ should have $n - 1$ electrons and so those with 10, 14, 18 and 22 electrons are predicted to be "aromatic". Maier's group has, in an elegant series of experimental studies,[18] obtained detailed spectroscopic data to confirm the original monocyclic-ring structural conjecture.[16] It is seems quite amazing to realize, in an age when we have complex Quantum Chemistry theories and massive computing power at our disposal, that the simple Hückel rule appears to works so well. Exhaustive ion-drift tube experiments by Bowers' group[19] have produced intriguing evidence for the existence of at least five different families of carbon species in the range C_n (n = 1–60). We thus conclude that we still have much to learn about pure carbon.

It came as quite a surprise, and indeed one which some refused to believe,[20] when in 1985 the claim was made that a third well-defined molecular cage form, C_{60} Buckminsterfullerene which had the same 12-pentagon and 20-hexagon pattern as a soccer ball, had self-assembled spontaneously from a hot chaotic carbon plasma. Although Osawa in 1970 had made the most imaginative conjecture that this molecule might be stable if it could be made his idea[21] remained almost completely unknown until the discovery paper[1] was published, partly perhaps because it was in Japanese. In addition David Jones in the New Scientist had, even earlier in 1966 under the pseudonym of Daedalus, hypothesised highly imaginatively over the possibility of creating such closed cages of any size in general by interspersing 12 pentagons within a graphene sheet.[22]

Although, as described above, the C_{60} discovery was made serendipitously during laboratory experiments which simulated the likely conditions in the atmospheres of cool red giant carbon stars to explain the abundance of carbon chains in space, there was a secondary aim. This was the conjecture that carbon chains might be the carriers of some mysterious and as yet unidentified astronomical spectroscopic features known as the Diffuse Interstellar Bands (DIBs). These features have puzzled scientists for some 90 years. The radioastronomy discoveries of carbon chains in space were made in collaboration with astronomers at the National Research Council in Canada using the telescope in Algonquin Park and it was during deliberations over the significance of this breakthrough that Douglas showed how carbon chain species might survive the harsh conditions in space and thus be possible carriers of the DIBs.[23] Interestingly the extraction and X-ray characterization by Krätschmer *et al.*[24] and our own (Sussex), essentially simultaneous, extraction and nmr characterisation of C_{60}[25] were both driven by aims to understand the origin of the DIBs as well as another mysterious feature known as the "217 nm hump". The 217 nm feature had long been an important focus for Huffman who had provided good laboratory evidence in the 1970's that it might be due to some form of carbonaceous dust.[26] In fact we now know that C_{60} can form under certain conditions quite efficiently in sooting flames but immediately destroyed as it attempts to pass through the flame barrier into an oxygen atmosphere. Indeed the Mitsubishi Corporation now produces C_{60} on an industrial scale by combustion of methane. Indeed the molecule appears to have been around almost everywhere and yet amazingly had remained undetected until nearly the end of the 20th Century. The fact that this third stable, well-defined, molecular form of carbon had been hiding in the shadows since time immemorial has always brought to (my) mind the mysterious character lurking in the dark streets and sewers of Vienna, made famous by Orson Welles in the classic movie "The Third Man".[27] On the basis of such revelations the likelihood that C_{60} must exist in space seemed overwhelming to me[28] as was the fascinating possibility that in some way, perhaps in the form of a derivative, it might also be responsible the DIBs.[29] We suggested that charge transfer bands belonging to complexes such as $[(C_{60})M]^+$ in which an atom of perhaps an abundant alkali or alkaline earth metal stuck to the surface of C_{60} might explain the DIB features.[29] Of course another possibility would be an endohedral $[M@C_{60}]^+$ species which seems less likely, but one never knows—with carbon anything is possible!

Especially thought-provoking support for the conjecture that C_{60} might exist in space lay in the fact that the original discovery was made, totally serendipitously, during laboratory experiments designed to simulate the chemical conditions in the outflows from cool red giant carbon stars. This conjecture received amazing confirmation in 2010 by Cami *et al.*[30] who have assigned infrared bands in the spectra obtained by NASA's Spitzer telescope of not only C_{60} but also C_{70}. What is really very surprising (at least to me) about this result is the fact that the only prominent features in the infrared region belong to these two fullerenes (Fig. 2).

There are what are called RCorBor stars in the atmospheres of which there is little or no hydrogen, mainly helium and carbon particles, and where I had conjectured C_{60} was most

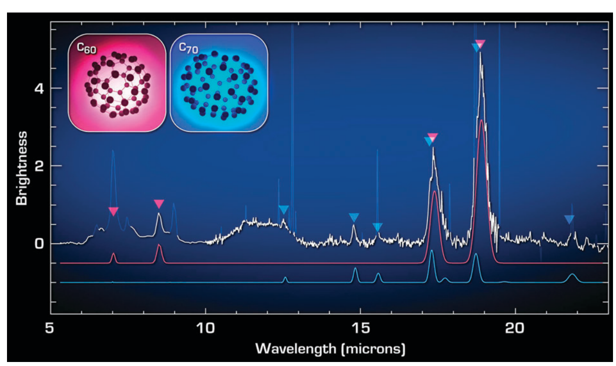

Fig. 2 The amazing NASA Spitzer telescope stellar infrared spectrum, published by Cami *et al.*,[30] in which the only clearly identifiable features belong to the fullerenes C_{60} and C_{70}. From J. Cami, B.-S. E. Peeters and S. E. Malek, Science 329, 1180–1182 (2010). Reprinted with permission from AAAS.

likely to be found and detectable but apparently there is significant hydrogen in the stars where C_{60} has been detected.[30] Prior to this finding it seemed almost inconceivable that chemical conditions might obtain in the atmosphere of such stars in which only these two species would be identifiable. The signatures appear in the so-called infrared "Fingerprint" region that has for decades been one of the most valuable for identifying molecules of all kinds. All these results, taken together suggest that the 90 year-old mystery of the carrier of the DIBs might be close to being resolved - at long last.

It just goes to show just how little we still know about many aspects of (pure!") carbon chemistry. In this period when fundamental science is yet again under threat and government is now pushing for almost all funding to focus on so-called "Strategic Science" there is particular reason to be thoughtful about the following facts: (a) There are scores of laboratories around the world studying hydrocarbon combustion and C_{60} was not discovered in any of them, (b) Nor was it predicted as a possible product of combustion which has been the subject of thousands of research programmes, moreover most importantly, (c) Some "experts" in the combustion field argued strenuously against not only the existence of C_{60} but also its importance in combustion.[31,32] Yet, as indicated above, Mitsubishi researchers have found combustion conditions in which the only molecular products are fullerenes. This is yet another example of the remarkably synergistic relationship between terrestrial and space science. In these difficult times this account indicates crucial value of "Blue Skies" or perhaps more accurately "Black Skies" cross-disciplinary research.

I have come to expect never to be surprised by the antics that C_{60} can get up to! When it was formed in 1660 the Royal Society deliberated over two possible mottos:[33] One was "Nullius in verba" which in context translates as "We take nobody's word for it". The second which the Society did not choose was "Quantum nescimus", which translates as "What a lot we don't know". As far as the first motto is concerned even today many, if not most, people unfortunately seem content to accept irrational claims for which there is no evidence and as far as the second is concerned it seems that it is just as true today as it was 350 years ago!

Acknowledgements

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