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Future studies on electron scattering; a renaissance

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Abstract. 2014 is the centenary of the first announcement of the Franck-Hertz experiment [1], now regarded as one of the pivotal experiments of modern physics.   The Franck-Hertz experiment is widely regarded as an experiment that provided validation of the Bohr theory of atomic structure, itself only published in 2013, however it should also be viewed as the first quantitative experiment in electron scattering and the birth of scientific study of atomic and molecular phenomena by collisions. Today we recognize that electron-atom and electron-molecule collisions are prevalent across nature, describing disparate phenomena whilst the exploitation of such collisions underpins many of the technologies upon which modern society relies. The centenary of the Franck-Hertz experiment is thus a suitable opportunity to review both our current knowledge of electron interactions and to consider the directions of future research. In this article I therefore aim to both review our current state of knowledge and look forward, proposing that recent advances are providing something of a renaissance to the field and are vital for emerging technologies as well as answering some of the greatest scientific challenges of the 21st century.

The Franck-Hertz Experiment

The original Franck-Hertz experiment [1], passed a beam of electrons through a vapour of mercury (interestingly described as mercury molecules) with subsequent detection of the kinetic energy of the transmitted electrons. A characteristic series of peaks were observed, separated by 4.9eV (254nm), precisely the energy needed to excite the first excited state of the mercury atom Figure 1. Thus an incident electron was described as scattering from the atom, transferring its kinetic energy to the target in exciting the atom. Hence by measuring the energy lost by scattering electrons it should be possible to determine excitation energies in the target and this is the basis of the now standard analytical technique of Electron Energy Loss Spectroscopy (EELS) capable of not only revealing electronic states but vibrational energy levels and, in some cases, even rotational structure. EELS is applied to gas phase targets providing a comparison with optical techniques [2] and is a standard technique in surface science [3] where it may be used to detect constituents of absorbates and may reveal surface phenomena such as plasmons. Electron spectroscopy in general is also used to explore ionization phenomena e.g. through photoelectron spectroscopy (PES) [4]. Thus the Frank Hertz experiment can be considered as the pioneer of energy loss spectroscopy.
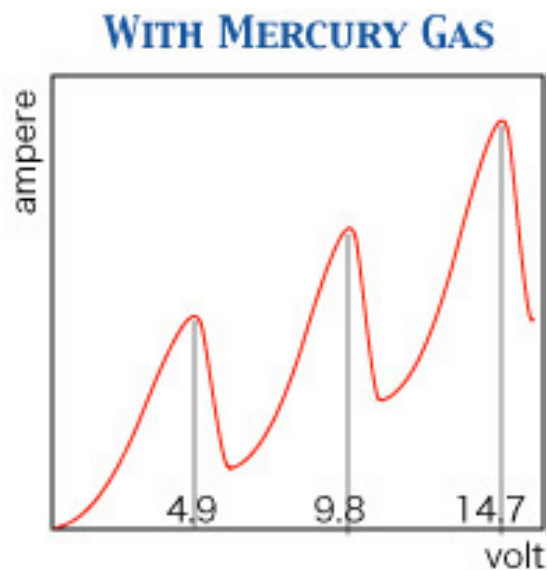
Figure 1. The typical Franck-Hertz electron curve showing the presence of a series of peaks separated by 4.9eV (254nm) characteristic of the excitation energy of the first electronic state of mercury.

Electron collisions and quantum mechanics

The 1920's are regarded as the decade in which quantum mechanics was born with the publication of the Schrodinger equation and the Heisenberg uncertainty principle. However what is often neglected is the role that electron collisions played in the development of the field. Once the true nature of the Franck-Hertz experiment was understood (the authors originally believing it to be an ionization phenomena), and due to both being called on to serve in WW1 this was not until 1919 with their award of the Nobel prize being in 1926, a series of electron transmission experiment were performed. Ramsauer [5] developed a more sophisticated apparatus using magnetic fields to collimate a beam of electrons whose energy could be more accurately defined (Figure 2a). At low energies (less than 1eV) when electrons passed through a chamber containing one of the heavier rare gases (Ar, Kr and Xe) the gas appeared to be 'transparent' with little or no scattering occurring, even for elastic scattering (figure 2b). Such a phenomena could not be explained by any classical theory which, from its 'billiard balls approach', would expect both scattering and at lower energies (longer interactions times) might expect a larger scattering cross section. However by applying the Schrodinger equation and considering the electron projectile as an incident wave composed of partial waves characterised by the momentum of the electron, this Ramsauer-Townsend minimum (Townsend conducting similar experiments at Oxford in the UK) could be explained. Accordingly quantum mechanics could be employed to study electron-atom/molecular interactions and calculate scattering cross sections which could be validated by experiment.

Thus it became possible to quantify electron collisions and use these cross sections to model natural and industrial phenomena. Led by Mott and Massey [6,7] in the UK the era of theoretical collision physics began. The first applications of this theory coincided with the technological development of radar and the discovery of the ionosphere. Ionospheric models and a physical description of that most magnificent of natural phenomena, the aurora, were based on theoretical descriptions and experimental measurement of electron-atom and electron-molecule collisions leading to excitation and ionization of the target species.
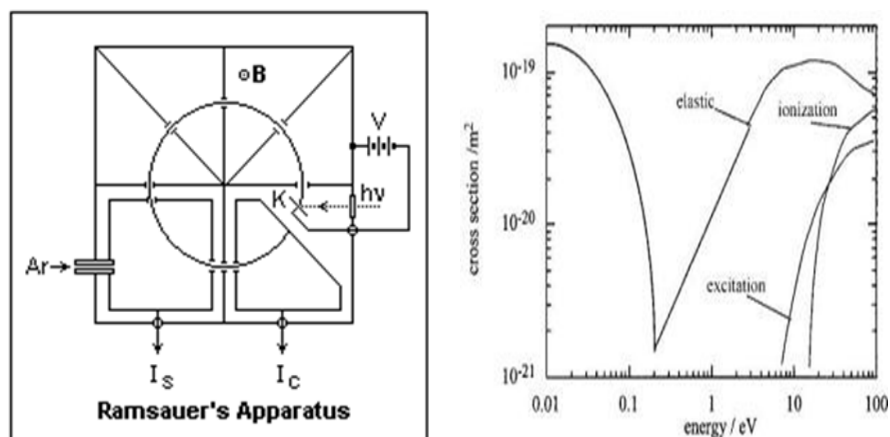
Figure 2. (a) The Ramsauer apparatus used to measure low energy scattering from atoms and molecules revealing (b) the Ramsauer-Townsend minimum in the total and elastic scattering cross section of the rare gases.

The first 'golden age' of electron collisions.
In the 1960's humanity, recovering from the destruction of the second world war, turned to science and in an unparalleled frenzy of activity supported scientific endeavours across the world. Many universities and research institutes were established in this period (hence the current plethora of 50 year anniversaries) and generations of new scientists were able to study the world providing an explosion of scientific data. Atomic and molecular physics was one discipline that enjoyed such a growth, indeed many of the now famous conference series (e.g. ICPEAC) were founded to disseminate this 'data explosion'. With new studies came new results as apparatus were developed to probe collision effects in greater detail. A major breakthrough came with the development of 'monochromated' electron beams, beams with resolution of less than 100meV capable of resolving vibrational structure in energy loss spectra. However such high resolution electron beams also revealed unexpected fine structures in collision cross sections for example a sharp dip in the elastic scattering cross section of electrons from helium at 19.317eV (Figure 3) [8].
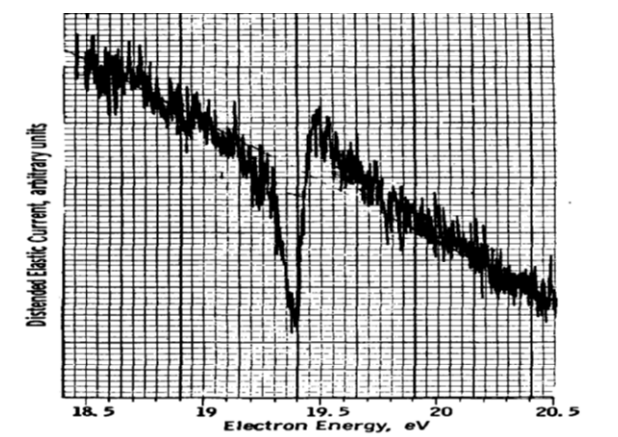

Figure 3. The original trace revealing the presence of resonances in electron scattering from helium [8].

Such a phenomena below the first excited state of helium (19.819eV) appeared to have no explanation but similar effects were seen in other atoms and molecules [9]. Schulz proposed that these 'resonances' could be explained if the electron was temporarily 'captured' by the target to form a 'temporary negative ion (TNI)' which lives for only a fs or ps before decaying by autodetachment hence performing delayed elastic scattering.

$$e + AB \rightarrow AB^- \rightarrow AB + e$$

Subsequent experiments, particularly in nitrogen [9], revealed that this effect may also leave the target excited, indeed such phenomena may dominate electron induced vibrational excitation.
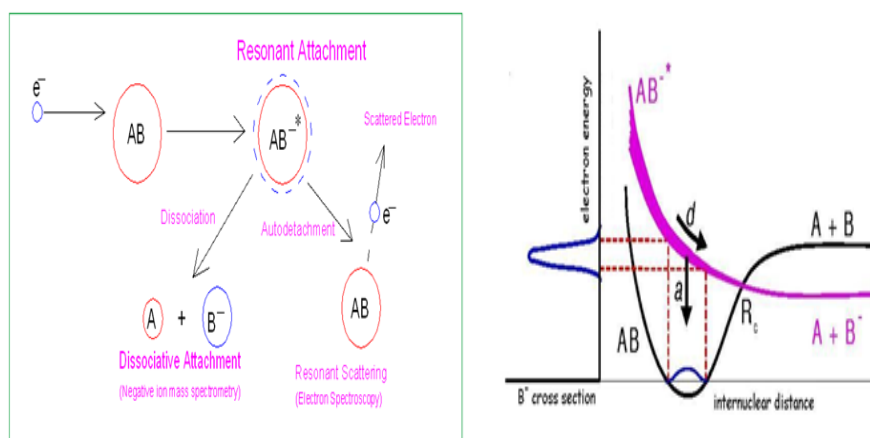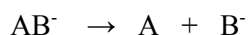

Figure 4. A schematic of the Dissociative Electron Attachment process (DEA) with an illustration of the potential energy surfaces f neutral and temporary negative ionic states [10].

An alternative route of decay leads to the fragmentation of the TNI to form an anionic product

$$AB^- \rightarrow A + B^-$$

a process entitled Dissociative Electron Attachment (DEA). First revealed in the 1960's it is a process common to most molecules though the probability (cross section) is low ($< 10^{-18}$ cm^2) [10]. However since the anionic product is charged it can be readily detected (e.g. by conventional mass spectrometry) and therefore was the subject of extensive studies. DEA cross sections are strongest for targets containing halogen atoms (since they are electronegative) but may be large in compounds containing 'psuedo-halogen' chemical groups such as –CN. DEA occurs naturally in the Earth's ionosphere where O$^-$ anions are formed by DEA to molecular oxygen.

DEA may be readily explained by an understanding of the potential energy surfaces of the anion and the neutral parent (Figure 4). The overlap of the anion curve and the neutral defining both the cross section and the residual kinetic energy of the product anions.

The desire to understand the dynamics of electron scattering led to ever more sophisticated experiments including study of electron-photon coincidences [11] to probe electron induced excitation (mainly of rare gases); electron-ion coincidence experiments [12] to explore electron induced ionization and correlation between incident, scattered and ejected electrons; the study of spin polarized electrons scattering from atoms and molecules [13] and electron scattering in the presence of laser fields[14] to couple electron scattering with photon excitation of the target (including study of 'electron induced de-excitation or 'super-elastic' scattering and simultaneous electron photon excitation). Such detailed experiments provided challenging tests of theoretical representations of electron collisions. Theory developed commensurate with the experimental progress coupling

quantum mechanical descriptions of the scattering with quantum chemistry descriptions of the target structures. Several 'formalisms' were developed and have stood the test of time with the R-matrix techniques [15], translated from nuclear physics perhaps being the most well known, although there are many other methods each with strengths and weaknesses and applicability to one scattering process over another, for a comprehensive review see [16].
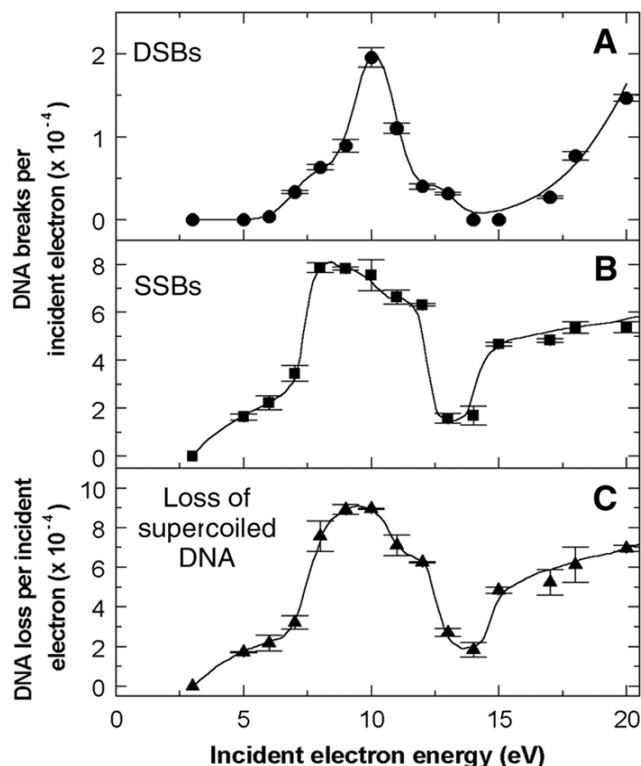

Figure 5. The now famous result of Sanche and co-workers showing resonance structure in electron interactions with DNA [22].

The new age.
In the late 1990's the study of electron collisions seemed to have reached a point where the community had gained an understanding of the collision processes that was sufficient and new challenges in atomic and molecular physics appeared to offer more intellectual and technical challenges (e.g. cold atom physics with the creation of BECs and ultrafast lasers capable of 'imaging' molecular dynamics). The collisions community began to contract and it seemed that the centenary of Franck-Hertz might deem the study of electron collisions as 'mission accomplished'. However, then a series of unrelated events made our need to understand electron interactions at the forefront of technology and the grand challenges of 21st century science.

In 1985 British Antarctic Survey scientists, Joseph Farman , Brian Gardiner, and Jonathan Shanklin reported massive falls in the terrestrial ozone layer in the Antarctic polar spring [17], levels collapsing by upwards of 90%. These were found to be due to a catalytic chemical reaction involving halogens (mainly chlorine) released by solar UV from chloroflourocarbons (CFCs) [18]. Many CFCs are purely manufactured and have no natural sources, indeed the first CFCs were created in 1928 as non-toxic, non-flamable refrigerants, and were first produced commercially in the 1930's by DuPont. The unfettered release of CFCs had led to a build up in their concentrations in the terrestrial atmosphere to such an extent that when they are photolysed the liberated free radicals can destroy many hundreds of ozone molecules before being destroyed themselves. This has led to the creation if the 'ozone hole'.
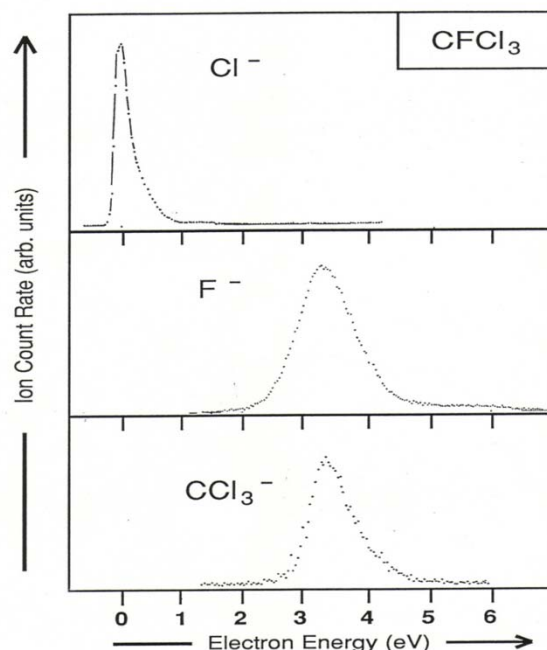
Figure 6. Demonstration of the ability of low energy electrons to selectivity cleave molecular bonds. At low energies (≈ 0eV) electrons cleave the C-Cl bond in CFCl₃ whilst at circa 3ev they cleave the C-Cl bond [25].

Simultaneously the observation that the Earth is warming, and at a faster rate than at any time humanity has been present, has led to major scientific and political debate [19]. Global warming arises from certain molecules in the atmosphere 'storing' energy released from the surface and re-radiating it back to the Earth's surface. The main molecules responsible for global warming are CO_2, methane and N_2O but, once again, many industrially produced compounds were found to have a high 'Global Warming Potential' (GWP) many of which also contained halogens so had a large 'ozone depletion potential' (ODP). Largely these halogenated compounds with large GWPs were used in plasma processing to etch surfaces (e.g. C_2F_6, C_3F_8, CF_4, SiF_4, C_5F_{12}, CHF_3, CCl_2F_2, SF_6, HF) [20]. One of the most important 'plasma etching' processes was to build the 'chips' used in computers, the power and speed of which is inversely proportional to the size of the etched phenomena, the smaller the size of the 'integrated circuit' the faster and more powerful the computer with technology development .

In the 1990's industry developing next generation integrated circuits was informed that worldwide governments were preparing to phase out CFCs in order to prevent the ozone layer being irreversibly damaged and to slow global warming. The plasma industry would have to find new 'feed gases' with which to etch silicon and hence fabricate 'computer chips'! However in most cases the actual physico-chemical processes in the plasma were unknown and in replacing existing feed gases with ones with lower GWPs/ODPs in existing plasma reactors the effects on the efficiency (and hence commercial viability) of the plasma reactor were unknown. This highlighted the need to model the plasma reactor and build 'virtual reactors' within which different feed gases could be trialed and etch rates and microstructures studied. Such models required basic electron collision data for many molecular species for which little or no data existed. Both US and Japanese industry sought to engage the international atomic and molecular community to provide such data [21] leading to a revival in both experimental and theoretical work, the latter being particularly relevant since many of the most important species in these plasmas are radicals (CF_x where x =1 to 3) which could not be studied experimentally.
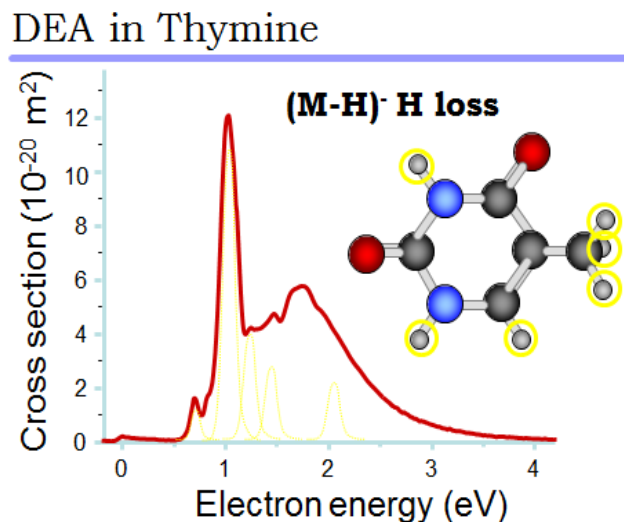
Figure 7. DEA to thymine illustrating selective bond cleavage using low energy electrons, H atoms are liberated from each site at distinct energies leading to fine structure in the DEA cross section [26].

The second field in which the study of electron collisions were found to be critical was radiation chemistry and the development of next generation 'radiotherapy'. In 2000 Sanche and co-workers published an astonishing result, they studied electron induced damage on stands of DNA [22]. The DNA helix can be ruptured in two ways one leading to a single strand break (ssbs), the other producing double strand breaks (dsbs). Sanche et al showed that, contrary to expectation, low energy (<10eV) electrons could produce both ssbs and dsbs and within these damage curves structures were revealed that are reminiscent of 'resonances' seen in electron-molecule scattering, figure 5. These results challenged many assumptions of the radiation chemistry community and our understanding of how DNA, the most important molecule in the cell nucleus, is damaged when irradiated by ionizing radiation. Instead of the primary radiation (X-ray, gamma ray, UV light) the secondary electrons produced by such radiation may induce 'direct' damage while also producing the free radicals that produce 'indirect damage'. Thus radiation chemistry and hence the models that underpin the radiotherapy protocols would need to be based on atomic and molecular interactions, operating on the nanoscale rather than the traditional macroscale picture. This led to an explosion of experimental studies that explored electron interactions with 'biomolecules' such as the nucleobases on which DNA is based   [23] and provided theory with enormous challenges to model electron interactions with such complex molecular targets [24].

Electron induced chemistry.
Both plasma and radiation chemistry studies revealed the important role of resonance phenomena in electron scattering and highlighted the role of DEA. In plasmas operating with halogen containing species DEA produced anions that meant the plasma was 'electronegative'. while the low lying resonances observed in electron scattering from biomolecules demonstrated that DEA could fragment the molecule and hence lead to DNA rupture. Furthermore DEA was found to be a 'bond specific process' and by controlling the energy of the incident electron it was possible to control the molecular fragmentation pathways - the 'holy grail' of chemistry for more than a century. Figures 6 and 7 illustrate this electron induced chemical control. In figure 6 very low energy electrons ($\approx$ 0eV) incident upon $CFCl_3$ are able to cleave the C-Cl bond exclusively (producing a Cl$^-$ anion and $CFCl_2$ neutral), whilst electrons at circa 3.2eV cleave the C-F bond with the electron being shared by the F and CCl_3 fragments [25].
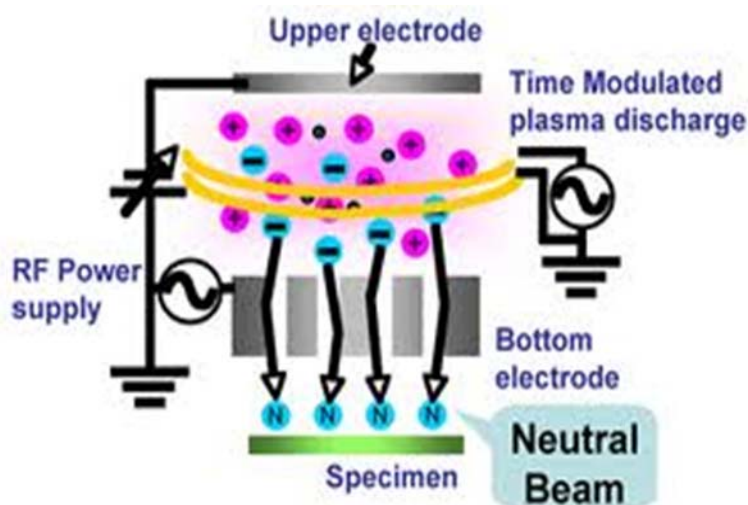
Figure 8. Schematic of a modulated plasma reactor that exploits electron induced chemistry to produce anions which are withdrawn from the plasma, charge exchanged with a carbon surface and then used to make a neutral beam for surface etching.

In biomolecules similar selective bond cleavage is observed, for example in thymine each of the bonds around the ring may be cleaved by electrons of a specific energy (figure 7) [26]. Accordingly is may be possible to design/select molecules that can be selectively fragmented to produce chemically reactive species that in turn produce new compounds or structures. Hence electrons may be the 'tool' for chemical control that femtosecond lasers and coherent control aimed to fulfil in last two decades of the 20th century and electron sources are much cheaper and more rugged that the complex laser systems used in coherent control.

The plasma industry was the first to exploit electron induced chemistry since the electron energy (temperature) in a plasma can be controlled by the voltages applied to the plasma generating electrodes. Samukawa and co-workers [27] demonstrated that, by pulsing the electrode voltages generating the plasma in an industrial etching reactor the electron temperature may be lowered and thus DEA channels opened, with the production of anions, Figure 8. These anions may be drawn out of the plasma and, by passing through a 'carbon filter', the anions converted to neutrals of the anionic species. Thus anions may be converted to neutral radicals which may then be used to etch the surface without the disadvantages of charging of the surface or UV damage from the plasma. Such neutral beam etching has been shown to produce well defined 20-30nm structures.

In radiation chemistry the recognition that DEA may play an important role in damage induced by ionizing radiation led to the proposal that molecules that have high DEA cross sections may be used as 'radiosensitizers' to increase the death of cancer cells [28]. Indeed many of the radiosensitizers' currently used in the clinic (such as bromouracil and cisplatin ($Cl_2H_6N_2Pt$)) contain halogenated species and thus have high DEA cross sections [29,30] – is this cause or effect ? New radiosensitizers have been proposed based on their DEA properties and ability to bind to DNA with higher probability of inducing ssb or dsb rupture when interacting with secondary electrons e.g 5-bromouridine and 5-nitrouracil [31,32]. More recently the introduction of metallic nanoparticles (normally gold or platinum) into cancer cells (ideally into the cell nucleus) has been suggested and tested with the expectation that such particles will be a ready source of secondary electrons which may then rupture DNA by DEA led processes [33,34].

This research is to be developed under a new pan-EU training network ARGENT [35]. Indeed electron induced processes are now being included in radiation damage modelling codes (e.g. LEPTS, GEANT4-DNA) which is a testimony to how far electron induced processes have been recognized

within the radiation chemistry community in the 14 years since the pioneering work of Sanche and co-workers.

Future electron studies

The ubiquitous nature of electrons in nature and in the technology we use means that the need to study and exploit electron induced collisions will continue unabated in the 21st century. The recognition that we no longer need to be passive spectators of the electron collision but may manipulate and exploit such processes is opening up new opportunities and will provide the motivation for much of the future research. For example in astronomy it is now clear that we live in a 'molecular universe' with rich (astro)chemistry present in regions of star and planet formation [36]. Indeed anions have been observed in such regions (C_xH^- and C_xN^-) [37] and it is possible that many of the more complex molecules found in these regions are produced by electron irradiation of the ice layers formed on dust grains, molecules that themselves may be essential for development of life (e.g. the assembly of DNA) [38]. The recent Cassini-Huygens mission to Saturn and its moons has revealed that Titan (considered by many to be a representation of early earth before life evolved) has a rich ionospheric chemistry with large concentrations of anions formed by DEA of the nitriles present in the upper atmosphere [39]. Similarly electron induced processes are important in upper atmosphere of Jupiter and Saturn where aurora have been observed.
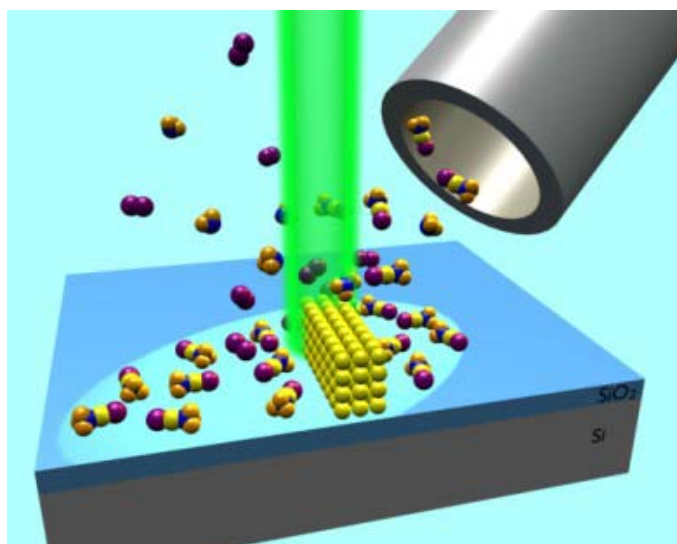

Figure 9. Schematic of the FEBID process in which a high energy beam of electrons (keV) irradiates a surface during deposition of a feed gas. Nanostructures are formed on the surface through electron induced dissociation and chemistry to the feed gas [42].

The next generation of electronic devices require even smaller (1nm or less) structures (transistors) to be created on surfaces. Such structures are apparently unable to be manufactured using current plasma etching techniques and require new methodologies. One such method is FEBID (Focused Electron Beam Induced Deposition) [40] in which a highly collimated beam of very high energy electrons is incident upon a substrate upon which a feed gas is directed, figure 9. These feed gases are typically large molecular compounds containing a metallic core. The electrons (or rather secondary electrons they liberate) release the metal by fragmenting the molecule and thus nm scale metallic structures can be fabricated. Central to this technology is the knowledge of electron interactions with the feed gas and how the electron induced chemistry both in the gas phase above the substrate and within the absorbate may be controlled to fashion the nanostructures, chemistry that is intriguingly different in the gas and solid (surface absorbate) phases [41]. Many of the feed gases proposed for

FEBID have never been studied before and are perhaps too large for current theoretical methods so have engendered a new set of experimental studies coordinated through the CELINA COST action [42].
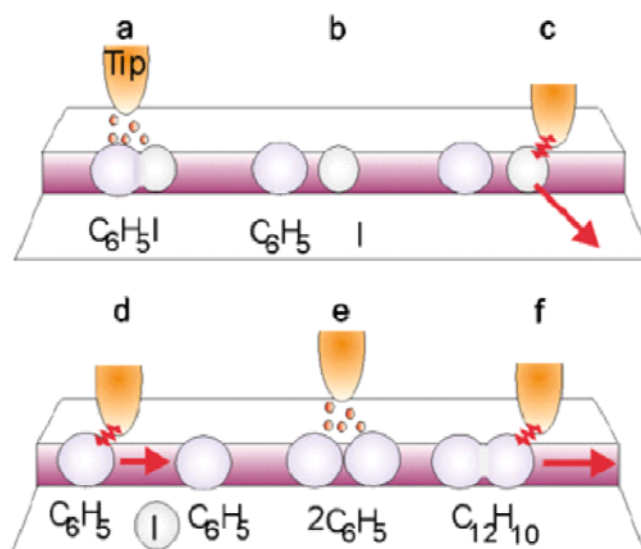

Figure 10. A STM is a bright electron source that may be used to induce chemistry on surfaces with the advantage that it may target one molecule as a specific spatial site. In this example it is used to fashion $C_{12}H_{10}$ from dissociation of C_6H_5I [44].

One of the major instrumental breakthroughs in the late 20th Century has been the development of the Scanning Tunnel Microscope (STM) allowing us to image atoms and molecules directly. A STM is *an electron source* and thus allows us to explore electron collisions in a new way. The 'electron beam' in a STM is highly focused and in terms of flux density very intense, indeed so intense that excitation of a molecule by two electrons is possible (analogous to two photon excitation in a strong laser field) [43]. However STM technology provides the opportunity to not only image the molecules but to move the molecules across the surface (e.g. to a reaction site) and may dissociate the molecule. The classic (and one of the earliest) example was the study of C_5H_5I (Figure 10) [44]. The STM electron 'beam' is used to cleave the molecule producing $C_5H_5 + I$ the C_5H_5 fragment may then be moved across the surface to meet a second C_5H_5 fragment and under the STM tip the two fragments combine to form $C_{10}H_{10}$. It is now known that the iodine fragment is most likely the I^- anion formed by DEA. Thus STM can induce electron chemistry with the added advantage that it can be induced in a specific site and even with a specific molecule. Thus, if electron chemistry can be combined with STM technology, the 'holy grail' of chemistry achieving site and spatial specificity may be achieved using electrons. Therefore in future it is to be expected (required) that studies of electron interactions will draw on members of the atomic and molecular physics, surface science and STM/nanotechnology communities to explore electron collision dynamics and, perhaps, lead to the construction of new structure/materials – though it is to be noted that STMs are 'low throughput' machines for any industrial fabrication.

Looking ahead other areas of science and technology that will engage with electron collisions include the space community. Electron collisions play an important role in space craft re-entry phenomena and were a major topic in the EU Phys4Entry project [45], with the development of commercialization of space (e.g. in asteroid mining and space tourism) such modeling will become increasingly relevant. It is also becoming recognized that electrons are present in large numbers in flames and thus that electron induced processes are important in combustion studies [46]. Indeed the correlation between compounds used as fire retardants and their large DEA cross sections has been

noted for some time [47]. Therefore one of the future areas ripe for development is exploration of electron chemistry in combustion.

Conclusions

In this review a brief history of the development of electron scattering from the pioneering experiment by Franck and Hertz a century ago to the resurgence of the field in the first decade of the 21st century has been presented. The discovery of the ability of electrons to cleave specific bonds in the target molecule has created a new opportunity to use electrons as a tool for controlling chemistry in different environments including plasma processing and radiotherapy. Electron induced chemistry is now believed to play an important role in chemical synthesis in space and in flames. Thus the study of electron collisions with an ever larger number of atomic and molecular targets will require the attention of many in the scientific community in the 21st century such that, on the occasion of the bicentenary of the Franck-Hertz experiment in 2114, it will still be seen as one of the great pioneering experiments in the history of Science founding the still active and exciting field of electron collisions.

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