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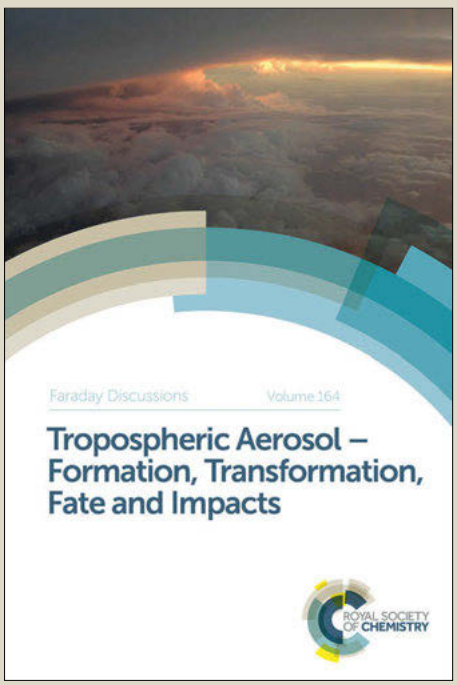


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# Electron Induced Chemistry A New Frontier in Astrochemistry

**Nigel J Mason[a], Binukumar Nair[a], Sohan Jheeta[a] and Ewelina Szymanska[a]**

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The commissioning of the ALMA array and the next generation of space telescopes heralds the dawn of a new age of Astronomy in which the role of chemistry in the interstellar medium, in star and planet formation may be quantified. A vital part of these studies will be to determine the molecular complexity in these seemingly hostile regions and explore how molecules are synthesised and survive. The current hypothesis is that many of these species are formed within the ice mantles on interstellar dust grains with irradiation by UV light or cosmic rays stimulating chemical reactions. However such irradiation releases many secondary electrons which may themselves induced chemistry. In this article we discuss the potential role of such electron induced chemistry and demonstrate, through some simple experiments, the rich molecular synthesis that this may lead to.

## 1 Introduction

The next decade promises to be the 'decade of astrochemistry' with recent discoveries preluding the impending explosion of chemical data from new telescopes (such as ALMA) that will reveal the 'molecular universe' [1]. The identification of now more than one hundred eighty molecular species in the InterStellar Medium (ISM) (HTTP://www.astro.uni- koeln.de/cdms/molecules, 2013) ranging from the simplest (and most abundant) diatomics $H_2$ and CO to the more complex organics (including aldehydes, esters and ketones) provides significant challenges to our understanding of chemistry under 'extreme conditions' that prevail in the ISM. The ISM is both cold (<10 K) and empty (pressures equivalent to $10^{-13}$ torr) such that it may appear that reaction rates will be slow even when two reactants collide in the vastness of space negating the probability of molecular assembly. Faced with this apparent misnomer a new hypothesis has been formulated that suggests chemical synthesis may occur on the surfaces of small (micron) sized dust grains found in the ISM (with about 1% abundance by mass). These dust grains act as 'chemical factories' accreting simple molecular material over the long lifetime of the ISM dust clouds ready for 'triggering' by an external energy source to form more complex molecules that subsequently are desorbed from the grain surface to be detected by terrestrial observations based on their spectroscopic signatures (in microwave, THz and IR). Direct reactions may occur when an impinging atom/molecule interacts with the icy surface e.g. the recombination of two H atoms $H + H \rightarrow H_2$ is believed to be the only method for forming the $H_2$ back ground that dominates space. Similarly hydrogenation of CO on dust grains may lead to the

formation of methanol in a four step process [2].

$$CO + H \rightarrow HCO \rightarrow H_2CO \rightarrow CH_3OH$$

However such routes are speculative and appear inefficient with many integrated steps being needed to create the large species such as cyanomethanimine NHCHCN and ethanamine, $CH_3CH_2NH_2$ recently identified using radioastronomy [3]. Since cyanomethanimine, is believed to be one step in the process that can lead to the nucleobase adenine, while ethanamine, is thought to play a role in forming alanine, one of the twenty amino acids in the genetic code, the presence of such complex species in the ISM suggests that prebiotic chemistry seeding life itself may start in the ISM and be an integral part of the star and planet formation process.

Ice covered dust grains in the ISM are embedded in the interstellar radiation field comprising of cosmic rays (90% of which are protons) and once dust clouds collapse to form a protostar may be subject to UV radiation. UV induced photochemistry has been the subject of extensive laboratory studies and demonstrates that irradiation of ice analogues may lead to the synthesis of complex (prebiotic) molecules including amino acids [4,5,6]. These studies traditionally have used lamp sources to mimic the ISM UV spectrum but more recently [7] have used synchrotron radiation to irradiate ice analogues demonstrating UV induced synthesis is both practical and wavelength dependent but the product yields were quite low.

*Table 1. Estimated UV photon and 1 MeV proton fluxes in different regions of space, and doses experienced by ices. Table adapted from [10].*

| Region | Residence Time of Ices in Region (years) | UV | | Cosmic Ray Photons | |
|---|---|---|---|---|---|
| | | Flux 10 eV photon eV $cm^{-2}$ $s^{-1}$ | Energy Dose eV $molecule^{-1}$ | Flux 1 MeV proton eV $cm^{-2}$ $s^{-1}$ | Energy Dose eV $molecule^{-1}$ |
| IS Cold dense cloud (0.02 μm ice) | $10^6$ $10^7$ | $1.4 \times 10^4$ | 0.4 4 | $1 \times 10^6$ | 0.3 3 |
| Oort cloud and KBO Region | $4.6 \times 10^9$ | $9.6 \times 10^8$ | $10^8$ (top 0.015 μm layer) | Energy dependent flux | 150 (0.1 μm) 55-5 (1-5 m) |
| Jovian Satellites e.g. Europa | $< 1 \times 10^8$ | $4 \times 10^{13}$ | $10^{13}$ (top 0.015 μm layer) | Magnetospheric ions $7.8 \times 10^{13}$ | 150 (1 cm $10^4$ years) |
| Typical Lab Experiment | $4.6 \times 10^{-4}$ | $8.6 \times 10^{14}$ | 14 | $7 \times 10^{10}$ | 9 |

Deeper in the cloud the UV field is weak and chemistry may be induced by deeper penetrating x-rays or cosmic rays (protons) which produce similar products as observed in UV radiation of the same ice, albeit with different (higher) yields [8]. The similarity in the products suggests that there may be a common chemistry occurring in such irradiation phenomena and it is now postulated that this may be chemistry induced by **electrons**. Secondary electrons are produced when any ionising radiation interacts with solid ices [9] indeed one high energy cosmic ray may release $10^4$ secondary electrons in its passage through a single ice covered dust grain, such electrons may themselves trigger chemistry with the mean kinetic energy of these electrons below 20 eV. Thus if we are to understand the synthesis of

complex molecular species in the ice mantles of dust grains in the ISM it is necessary to understand the chemistry induced by the most abundant species in any ice processing – electrons and often low energy electrons close to the ionisation potential of any absorbed molecular species. In this paper we will explore typical chemistry induced by electrons within thin layers of ice mantle as experienced on dust grains in the ISM.

## 2 Experimental Apparatus

The electron irradiation experiments described in this paper were performed inside an ultra-high vacuum (UHV) chamber at the Molecular Physics Laboratory at the Open University at Milton Keynes, UK. Figure 1 presents a schematic illustration of the employed experimental setup. The chamber aims to simulate the physical conditions in the ISM by providing a base pressure of below $2 \times 10^{-8}$ mbar, with the residual gas being mainly molecular hydrogen, as in the ISM. A clean ZnSe substrate cooled by a closed cycle He cryostat system provides a surface on which ISM analogues may be prepared by 'background' deposition. The vapour is being introduced at a rate of $1 \times 10^{-6}$ mbar for 300 seconds. Typically ice layers are formed at 14 K and are amorphous in nature. The substrate may be heated to initiate phase changes (from amorphous to crystalline ice) and to initiate Temperature Programmed Desorption (TPD) to analyse the products of electron irradiation. The ice samples may also be analysed in situ by Fourier transform infrared (FTIR) spectrometry using a NICOLET FTIR spectrometer operating in the 3500 – 800 $cm^{-1}$ region with a spectral resolution of 2 $cm^{-1}$. Infrared spectra of clean substrates were acquired before each experiment for background correction purposes.

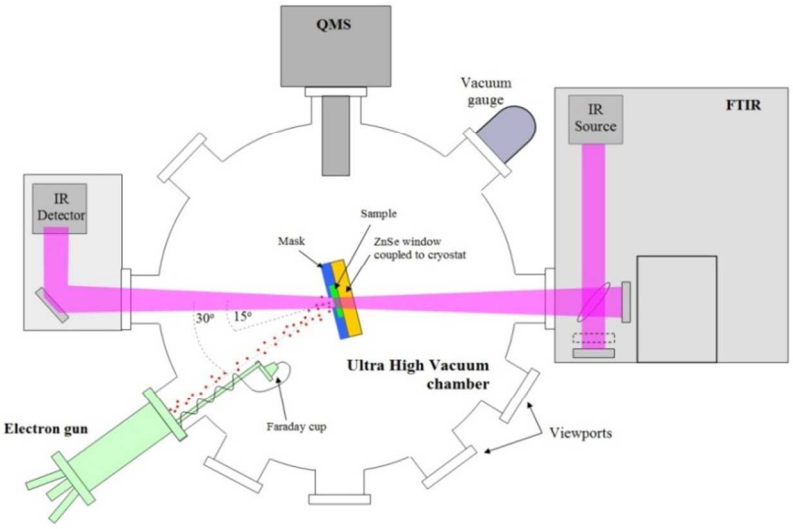


*Figure 1. Schematic diagram of the experimental apparatus used in the electron irradiation experiments. See text for details.*

Irradiation of the ice samples was performed by a collimated electron beam with generated from a Kimball Physics electron gun. The electron beam current was measured with a Faraday cup mounted at the end of the electron gun. The bombarded area was about 0.28 $cm^2$ and the beam current at the sample was estimated to be 1.7 μA ~ $10^{13}$ electrons $s^{-1}$. The employed electron flux at the sample was roughly 3.7 × $10^{13}$ electron $cm^{-2}s^{-1}$ (2.3 × $10^{15}$ electrons $cm^{-2}$ $minute^{-1}$). This flux is much higher than that encountered in any astrophysical context for example the electron flux at the Earth orbit is about 1 × $10^7$ electrons $cm^{-2}$ $s^{-1}$ [11] such that one minute of irradiation in the laboratory corresponds to roughly 6 years in space outside the Earth's atmosphere.

In the present set of experiments we used 100 - 5 keV electrons to irradiate the ices. The penetration depth of 2 keV electrons may be estimated using Monte Carlo simulations drawn from the CASSINO code [12]. The penetration depth (for 95% of the beam) is around 100 nm resulting in a LET (Linear Energy Transfer) of roughly 20 keV $m^{-1}$. For the employed electron flux, and assuming a typical sample density of 1.16 g cm-3, the energy delivered by the beam into the sample every second (ice layers within the first 100 nm) was about 0.8 eV $molecule^{-1}$. This value is the same amount of energy delivered by cosmic rays, to a typical interstellar ice grain over the few billions ($10^9$) of years that a dust grain is expected to survive. Thus in the present experiments we may deposit as much energy into the irradiated ice as a typical ice covered dust grain in the ISM may receive in its entire life cycle. Thus we must be aware that in astrochemistry analogue experiments (with photons or electrons) we are greatly enhancing the molecular synthesis rates that occur in these regions. In mitigation it should however be noted that once/as a protostar forms there may be a period of more intense bombardment by such particles.

## 3. Electron induced molecular synthesis

### 3.1 $O_2$ ice films

As a first, simple, example of electron induced synthesis consider a pure film of molecular oxygen [13,14]. Irradiation of such a film by electrons with energies above ~10 eV leads to the dissociation of molecular oxygen to release reactive O atoms which can react with remaining $O_2$ species. What follows is characteristic of the well know chemistry in the Earth's stratosphere.

$$O + O_2 + M \rightarrow O_3 + M$$

The formation of ozone requiring the presence of a 'third body' M to stabilise the highly excited nascent ozone. In the Earth's stratosphere M is commonly $N_2$ or another $O_2$ and thus ozone formation is limited to lower altitudes where the probability of a three body reaction is sufficient. In contrast in a solid film M maybe the surface itself or neighbouring molecules. Hence rates of ozone formation in solid ice film are high. Further details on the dynamics of such molecular synthesis may be determined by using a mixture of $^{16}O_2$ and $^{18}O_2$ leading to the formation of many different isotopologues of ozone (Figure 2) [14].

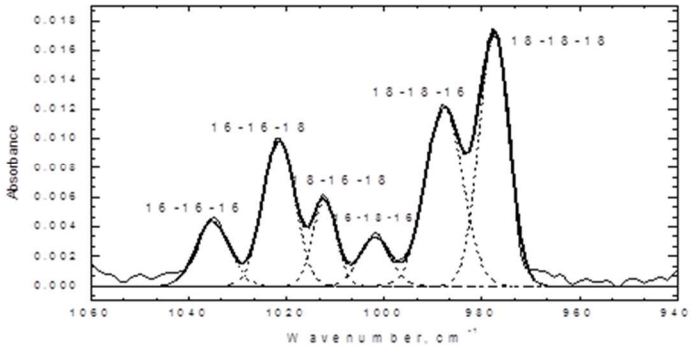


*Figure 2. The formation of six ozone isotopomers and isotopologues, $^{16}O^{16}O^{16}O$, $^{18}O^{18}O^{18}O$, $^{16}O^{16}O^{18}O$, $^{18}O^{18}O^{16}O$, $^{16}O^{18}O^{16}O$, and $^{18}O^{16}O^{18}O$, has been studied in electron-irradiated solid oxygen $^{16}O_2$ and $^{18}O_2$ (1 : 1) ice at 11 K.*

This simple experiment demonstrates many key features of electron ice irradiation experiments. It is efficient (ozone yields are observed as soon as irradiation starts) and depends strongly on temperature of the ice which influences the mobility of product reactants, indeed if the ice is left dormant after a period of irradiation at a low temperature (14 K) (e.g. for an hour) and then subsequently warmed ozone yields increase during the warming since O atoms trapped in the irradiated ice become mobile and react away from the site of their original production [13]. Similarly in space a radical released by one cosmic ray may remain dormant in the ice for long periods until another reactive species is produced in a second irradiation event or until the grain is warmed (e.g. by a shock wave) [15]. Ice covered dust grains have therefore been entitled 'radical bombs' with the energy released by such reactions leading to the desorption of products from the surface so they may be observed. Such observations also pose questions as to the validity of simple TPD as a method for determining products of irradiation since the TPD warming may itself initiate radical reactions and therefore a combination of in site (FTIR) studies of the irradiated ice with TPD is recommended for such astrochemical studies.

The temperature dependence of the product yields may also be counter intuitive. The ozone monomer column density is highest in ices prepared at the lowest temperature of 11 K (Figure 3) while the column density of the [$O_3$...O] complex rises as the temperature of the oxygen matrix is increased. This may be due to the nascent $O_2$ being in the form of weakly bound dimers ($O_4$) with O + $O_2$ reaction occurring within the dimer, a process more commonly called an 'intercluster' reaction in contrast to at higher temperatures were the dimer is unstable and the ice may be treated as independent $O_2$ molecules in a solid ice matrix [13,14].

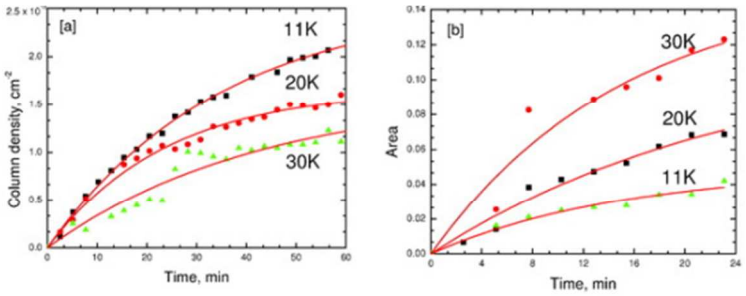


*Figure 3. (a) Temporal growth of the column density of the ozone monomer. (b) Temporal growth of the [$O_3$...O] complex.*

Having reviewed the possible physico-chemical processes that may occur in the irradiation of ices we will now illustrate the variety of electron induced chemistry that may occur in some simple ISM ice analogues.

### 3.2 Irradiation of methanol ice

Methanol ($CH_3OH$) has been detected through infrared spectroscopy in some low- and high-mass protostars such as W33A and RAFGL 7009, and also in comets, as Hale-Bopp and other Solar system bodies, such as 5145 Pholus a centaur planetoid. It is the sixth most abundant molecule after $H_2O$, CO, $CO_2$, $NH_3$ and $O_2$ in protostars (~6 %) and comets (~2 %) such that it proposed to be an important precursor of more complex prebiotic molecules the synthesis of which may be induced by UV or cosmic ray bombardment.

Figure 4 shows the production of CO and $CO_2$ from electron irradiation of methanol. The products and yields show little energy dependence (100 eV, 1 keV or 5 keV) producing very similar yields suggesting that the bulk of the formation is induced by lower energy electrons as the incident electrons thermalize in the ice, indeed these results are in good agreement with the low energy electron experimental data [16,17].

Figure 4 also shows that ice modification begins to take place almost immediately upon irradiation the $^{12}CO_2$ column density being lower than that of $^{12}CO$ as might be expected if CO liberated from $CH_3OH$ is a precursor to $CO_2$ formation. Other products readily detected by FTIR spectroscopy of the ice are $H_2CO$ and $CH_4$ demonstrating a rich chemistry in the ice film upon electron irradiation. The loss of nascent methanol is shown to be reflected in the formation of these products in a conservation of total molecular mass (Figure 5). Irradiation products gradually increase in concentration until they are present with sufficient intensity that they in turn are dissociated by irradiating electrons, this is demonstrated in the measured $CH_4$ yield (Figure 6) where after a fluence of ~1.8 e/cm$^2$ a reduction in the product methane is observed. A very similar destruction curve for $CH_4$ was observed by Hudson et al [18] and Barrata et al [19].

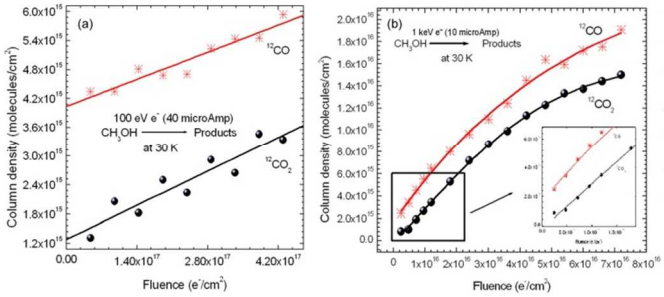


*Figure 4. Formation of CO and $CO_2$ by electron irradiation of a 30 K solid methanol ice film by (a) 100 eV and (b) 1 keV electron beam.*

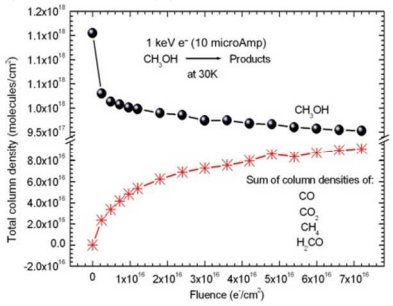


*Figure 5. Destruction rate of the $CH_3OH$ compared with the summed formation of CO, $CO_2$ $H_2CO$ and $CH_4$ products during irradiation of a 30 K solid methanol ice film by 1 keV electrons.*

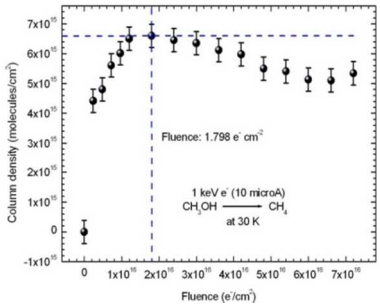


*Figure 6. The column density of $CH_4$ formed during electron irradiation of a 30 K methanol ice.*

### 3.3 Irradiation of a mixed methanol/ammonia ice

In the ISM the ice grain mantles will be a complex mixture of ices. The richer the ice composition the more varied the species produced. As a simple example of the range and complexity of the chemistry that may occur in such an irradiated ice mixture we examined electron irradiation of a 1:1 mixture of ammonia:methanol. Ammonia is prevalent across the ISM in protostars, comets and on the surface of many planetary bodies indeed it is now postulated that a large part of the nitrogen available to the early solar system was in the form of highly fractionated ammonia [20]. Once again high yields of CO and $CO_2$ are observed (Figure 7) but in contrast to pure films of methanol the $CO_2$ column densities are higher than that of CO since the CO produced is being utilised to make other compounds such as isocyanic acid

(HNCO), formed from combining the product of $NH_3$ dissociation ($NH_2$ radical) with CO.

$$NH_3 \rightarrow NH_2 + H$$

$$NH_2 + CO \rightarrow HNCO + H$$

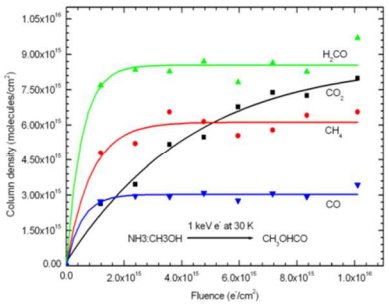


*Figure 7. Product yields measured during irradiation of a 30K $NH_3$:$CH_3OH$ ice by 1 keV electrons.*

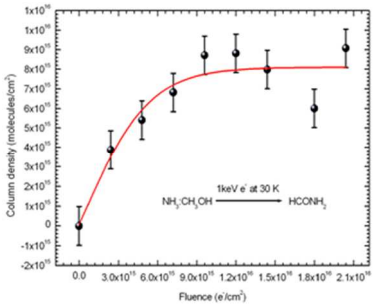


*Figure 8. The formation of formamide during irradiation of a 30K NH3:CH3OH ice by 1 keV electrons.*

Prior to the irradiation of the $NH_3$:$CH_3OH$ film we hypothesised that we may observe methyl amine ($CH_3NH_2$) by the following route but no signature of this molecule was observed in contrast strong yields of formamide $HCONH_2$ were observed (Figure 8). $HCONH_2$ can be formed from the reaction of $NH_3$ with formic acid (HCOOH) or methyl formate ($CH_3OHCO$), which is a product of esterification of $CH_3OH$ and HCOOH.

$$HCOOH + NH_3 \rightarrow HCONH_2 + H_2O$$

and/or

$$2\ CH_3OHCO + 2\ NH_3 \rightarrow 2\ HCONH_2 + 2\ H_2CO + H_2$$

Formic acid and methyl formate (which may also be formed by irradiation of pure methanol ice films [21]) were both observed in this experimental study during the irradiation of $NH_3$:$CH_3OH$ and once again reveal the complexity of the electron induced chemistry even in a simple binary ice. It is thought that during 'chemical evolution' $HCONH_2$ may have been used as an informational polymer since, under

certain conditions, it can form acyclonucleosides [22]. These then combine base purines and pyrimidines to yield acyclonucleotide which could have played a role very similar to the part played by RNA as a repository vehicle for genetic information in the 'RNA world hypothesis. Thus even in a simple binary ice the ingredients for biochemistry may be readily formed by simple electron irradiation.

## 4. Electron Induced Anion Chemistry

One of the most exciting developments in recent molecular physics has been the discovery that Low Energy Electrons (LEE) may not only dissociate the molecular target but may do so at well defined reaction sites often leading to almost 100% bond selectivity thence initiating controlled chemical processing in the local environment. The process by which LEE can induce such bond selective molecular fragmentation is known as Dissociative Electron Attachment (DEA) (Figure 9). An incident electron may be captured by the molecular target (XY) to form an excited state of the molecular negative ion $XY^{\#}$. This state, commonly called a Temporary Negative Ion (TNI), generally decays by ejecting the excess electron within a finite time depending on its lifetime (a process called autodetachment) but the molecular negative ion may also decay through dissociation leading to the formation of a stable negative ion $X^-$ and a neutral (often radical) fragment (Y) a 'reaction' summarized as $e^- + XY \rightarrow XY^{\#-} \rightarrow X^- + Y$. In contrast to direct electron impact, where the incident electron must have an energy of several eV to dissociate a molecule, DEA can dissociate a molecule at energies below the dissociation energy of the ground state. In numerous cases DEA effectively occurs at electron impact energies of a few meV, that is at thermal energies (kT) and generally, these low energy processes have very large cross-sections of 100s to 1000s of $Å^2$ which are much larger than cross sections for direct electron (or photon) induced dissociation discussed above.

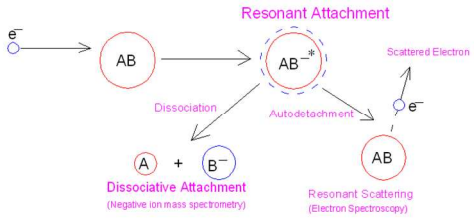


*Figure 9. Schematic of the DEA process*

Should DEA occur in a dense media such as in the condensed phase, within a surface layer or within a cluster the neutral and generally more highly reactive products produced by DEA (Y) may then initiate further chemistry through reactions with neighbouring molecules (AB) i.e. Y+ AB → AY+ B. As an example consider a mixed cluster of $NF_3$ and $CH_3Cl$ (Figure 10). The cross section for $Cl^-$ production from $CH_3Cl$ by direct electron impact is negligible < $10^{-23}$ $cm^2$. However $F^-$ ions may be liberated from $NF_3$ may react with $CH_3Cl$ by the well known nucleophilic displacement ($SN_2$) reaction $F^- + CH_3Cl \rightarrow CH_3F + Cl^-$ [23]. We thus form $CH_3F$ on a surface in a mixed multilayer of co-deposited $CH_3Cl$ and $NF_3$ (Figure 10). The $Cl^-$ ions can then be liberated/desorbed from the film and the synthesized molecular species $CH_3F$ left on the surface. Thus DEA may lead to direct (and total) chemical

transformation of the surface.

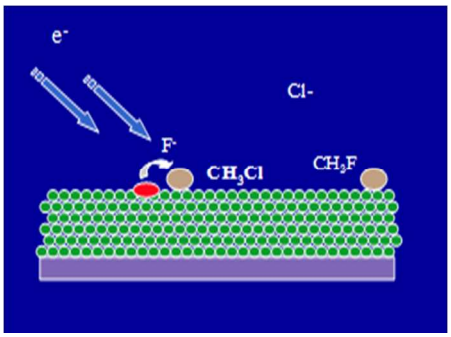


*Figure 10. Electron induced $SN_2$ reaction of $NF_3$ and $CH_3Cl$ molecules on a surface.*

The role of DEA in ISM dust grain chemistry has yet to be quantified indeed until 2006, it was not known if anions existed in the ISM. However, the possible existence of detectable abundances of anions in the ISM had been discussed for more than two decades and even included in a chemical model of the envelope of IRC +10216. In particular, Millar et al. [24] predicted an abundance of $C_8H^-$ as large as a quarter of that of its neutral counterpart $C_8H$ in the outer envelope of the C-star IRC +10216, a source known to be particularly rich in C-chain molecules. Recently, the first anion $C_6H^-$ anion was detected based on laboratory work [25]. Subsequently, all linear carbon chain anions with large electron affinities: $C_8H^-$, $C_6H^-$, $C_4H^-$, $C_5N^-$, $C_3N^-$ and $CN^-$ have been identified in one or more sources in the Universe, including dark cloud core TMC-1, the prestellar core L1544, the circumstellar shell of the AGB star IRC+10216, and the protostellar objects L1521F and L1527.

Since the binding energy of an electron to a neutral species, known as the electron affinity, is typically smaller in energy than a chemical bond, DEA is normally endothermic [26] e.g.,

$$HCCCN + e^- \rightarrow CCCN^- + H$$

In order for DEA to be exothermic and so occur at low temperatures of the ISM, there must exist weak chemical bonds in the neutral precursor. Several such processes have been discussed in the astrophysical literature. Petrie [27] realized that the formation of $CN^-$ could occur via the exothermic reaction,

$$MgNC + e^- \rightarrow CN^- + Mg$$

from the precursor neutral MgNC, which has been detected in IRC +10216. Sakai et al. [28] calculated that the anion $C_6H-$ can be formed from $C_6H_2$

$$C_6H_2 + e^- \rightarrow C_6H^- + H$$

a reaction that is exothermic by 16 kJ $mol^{-1}$. Herbst and Osamura [29] calculated that the corresponding reaction to form the anion $C_8H^-$, $C_8H_2 + e^- \rightarrow C_8H^- + H$ is exothermic by 47 kJ $mol^{-1}$.

DEA electron induced anion formation processes are now therefore now being included in the astrochemical models and new data on the DEA to ISM molecular species are being assembled [30-31]. However, dipolar dissociation (DD) also known as ion pair formation is another electron induced anion formation process and should also be included in astrochemical models

$$e^- + AB \rightarrow AB^* + e \rightarrow A^- + B^+ + e^- \quad ,$$

and to date is only quantified for a very small number of hydrocarbons [31]. Figure 11 presents anion yields for the formation of three groups of fragments: $H^-$, $C^-/CH^-$, and $C_2^-/C_2H^-$ via LEE interaction to acetylene, while the $C^-/CH^-$ anions are only formed by DD. Furthermore, DD yields may contribute > 30% of total anion yield along primary radiation (keV) tracks.

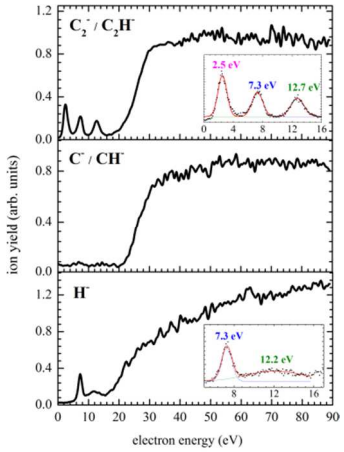


*Figure 11. Anion yields for acetylene as a function of electron energy. The inset shows the anion yield at low electron energies. The resonance peak position was determined by Gaussian fitting.*

## 5. Conclusions

The commissioning of the ALMA array and the next generation of space telescopes (led by JWST) heralds the dawn of a new age of astronomy in which the role of chemistry in the interstellar medium, in star and planet formation may be quantified. A vital part of these studies will be to determine the molecular complexity in these seemingly hostile regions and explore how molecules are synthesised and survive. The current hypothesis is that many of these species are formed within the e ice mantles on interstellar dust grains with irradiation by UV light or cosmic rays stimulating chemical reactions leading to larger more complex molecular species including those that may be the 'prebiotic' precursors. However such irradiation releases many secondary electrons which may themselves induced chemistry. In this article we have discussed the potential role of such electron induced chemistry and illustrated, through some simple experiments, the rich molecular synthesis that electron irradiation of dust grain ice analogues may produce. It is necessary to further quantify the role of such electron chemistry and determine whether photon

and cosmic ray (ion) bombardment is better understood as chemistry induced by the secondary electrons produced from the primary (UV /ion) species during its 'absorption' in the ice mantle. Furthermore the discovery that low energy (sub ionisation energy) electrons can induce chemistry through the process of dissociative electron attachment needs to be reflected in astrochemistry models, particularly now that anions have been detected in space. The astrochemistry community therefore should also the radiation chemistry community exploring DNA damage where, since the pioneering work of Sanche and co-workers [32] in 2000 it has become apparent that electron induced damage may be the major mechanism for direct damage in cellular systems [33]. The field of electron induced chemistry as an industrial tool for surface engineering is also developing rapidly and once again the astrochemistry community can and should assimilate data from this community relevant to their research. In this year of the centenary of the Frank Hertz Experiment it is perhaps fitting to recognise the ubiquitous nature of electron collisions and how they influence the world (and universe) around us.

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[a] *The Department of Physical Sciences and CEPSAR, The Open University, Walton Hall, Milton Keynes, MK7 6AA, United Kingdom. Fax: 00 441908 6554192; Tel: 44 1908 655253; E-mail:* nigel.mason@open.ac.uk

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