Electron controlled chemistry

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Abstract. The role of dissociative electron attachment in controlling electron induced chemical processes is discussed in terms of the unique characteristics of this process. The selectivity of molecular dissociation that exists in the gas phase using low energy electrons alone or in combination with laser excitation and in condensed phase are described and recent efforts in chemical control using electrons are summarized.

1. Introduction
It is by now established that free electrons are the facilitators of all chemical reactions that take place in plasmas. The interaction of free electrons with atoms and molecules lead to the formation of excited species, ions and radicals [1, 2] which then reacts among themselves or with atoms and molecules in their ground or excited states to produce new species. In many of these reactions, the role of electrons is not only in providing the necessary energy to overcome the barrier for a reaction, but also in creating a pathway which may not have been possible otherwise. A wide variety of processing plasmas used for various industrial purposes like lighting, semiconductor etching, plasma assisted chemical vapour deposition and high temperature resistant coatings and paints, gas lasers, pollution control and nanolithography are examples where the electron induced chemical reactions play the decisive role. It is also realized that the electron induced processes are the inevitable links in the creation of molecules, including biological molecules in interstellar medium and radiation damage in biological systems. In most of these situations, it is the process of dissociative electron attachment (DEA) that plays a crucial role. The DEA process occurs through a resonant capture of the electron by the molecule and the unique characteristics of the formation and decay of the resonance give rise to possible control of the dissociation of the molecule. There is a fast growing body literature which deals with dynamics of this process at the individual molecule level in gas phase and in condensed phase, in the form of thin films, adsorbed on surfaces as single species or mixed, and in the form of mixed clusters. All these are headed towards better understanding of electron induced processes and ways of controlling it for specific applications.

2. Chemical control through DEA
The negative ion resonance formed in electron-molecule collision can decay either through electron ejection or through dissociation. The decay of these negative ion resonances through autodetachment generally leads to vibrationally or electronically excited states of molecules, many of which (like high vibrational level excitation and spin forbidden transitions) may not be possible through the direct scattering process. If the life time against autodetachment is long enough and the potential energy surface is repulsive, the resonance may decay through dissociation yielding a stable negative ion and a
neutral fragment. The entire process starting from the formation of the resonance and its subsequent
dissociation to form a stable negative ion is called dissociative electron attachment (DEA). The
process of DEA has several unique properties which allow selective chemical transformations. These
are the kinematics, the decay dynamics and the selection rules.

The most striking feature of electron collision on molecules which lead to DEA is that even
near zero energy electrons can dissociate a large number of molecules. This has to be clearly
contrasted with photon processes, where the photons need a minimum energy equal to the bond
dissociation energy to break a molecule. This unique feature of electron collisions arises from the
positive electron affinity of many atomic and molecular species which allows the dissociation limit of
the negative ion resonance to be lower than the ground state energy of the neutral molecule. The
minimum energy requirement for the DEA process is obtained by subtracting the relevant electron
affinity (EA) from the bond dissociation energy ($D_0$). Depending on $D_0$ and EA, the minimum energy
could even be negative. Since DEA deals with free electrons, the minimum energy in this case would
be zero energy. However, the negative sign of the minimum energy signifies that the molecule could
even capture a bound electron from another species, e.g. a Rydberg state, and undergo dissociation [3].
For a given molecule, depending on $D_0$ of the particular bond and the electron affinity of the fragment,
there will be distinct threshold energies for various fragmentation channels. The distinct thresholds for
different channels give a handle on breaking the molecule selectively using the electron energy as a
control parameter.

![Figure 1. Schematic of DEA from a molecule in vibrational excited state as compared to the
ground vibrational level.](image)

After its formation, the negative ion resonance could decay either through autodetachment or
through dissociation. Both the dissociation time and the electron detachment time are functions of the
inter-nuclear co-ordinates. As shown by O’Malley [4], the DEA cross section is an exponential
function of the ratio of the two time scales – the autodetachment time and the dissociation time. The
exponential dependence on the timescales allows dramatic changes in the DEA cross section by
altering the Franck-Condon overlap region between the neutral molecule and the resonance. This is
shown in figure 1 for the case of a hypothetical molecule AB. When the molecule is in the vibrational
ground state at the time of capture, the resonance takes a time $\tau_d$ to cross the internuclear distance $R_c$


beyond which it cannot decay by electron ejection and thus has to necessarily dissociate. When the
molecule is vibrationally excited, the Franck-Condon region extends over larger internuclear distance.
The electron capture occurring at the right turning point of the vibration leaves the resonance very
close to $R_c$, when $\tau_d$ is very small $\tau_a$ is larger. This could lead to several orders of magnitude increase in
the DEA cross section as observed in the case of heated gases [1, 2] and Na$_2$ molecules selectively
prepared in high vibrational levels [5]. This behaviour provides a way for mode selective chemistry.
What is needed is the selective excitation of the vibrational mode in a molecule using a laser followed
by collision of electrons of appropriate energy. However, very few experiments have been reported in
this respect, mainly due to the problems in preparing the molecules in excited vibrational levels with
sufficient target densities.
While pure vibrational excitation provides a way for controlling the DEA process, electronic excitation also provide ways of controlling the DEA process. The electronic excitation leads to change in quantal state, shape, size and symmetry of the molecules. The change in shape and size generally leads to increased extent of the electron cloud as well changes in bond distances. Electronic excitation also increases the polarizability of the molecule which is the dominant term in the electron–molecule interaction potential. All these factors lead to changes in the capture cross section. In addition, structural changes as well as vibrational excitation that accompany electronic excitation lead to change in the Franck-Condon overlap regions considerably. The effect due to this would be similar to or far more dramatic than what is seen with pure vibrational excitation. The change in symmetry of a molecule may also lead to extensive changes in the DEA process due to the symmetry based selection rules in the electron capture process [6]. Hence change in symmetry through electronic excitation may lead to opening up a new channel or closing an existing one [7]. In short, electronic excitation followed by electron collision offer a means of controlling molecular dissociation.

So far we discussed the case of isolated molecules in a gaseous medium. What about the possibility of controlling electron induced processes when they are in aggregation, like in a cluster or in condensed phase? It is seen that the negative ion resonances in molecules are formed even when they are condensed on a surface [8]. However, the DEA process is considerably modified by the environment starting with the change in symmetry of the molecule due to the presence of the neighbouring atoms or molecules [9, 10]. In addition to this, changes in the capture probability, lifetime, energy and decay channels of the resonance could be modified in the condensed phase. For molecules adsorbed on a well ordered substrate, the preferential orientation could play a decisive role in the capture probability due to the symmetry rules. Charge transfer between the negative ion resonance and various elements of their local environment are also seen to affect the resonance properties and DEA cross sections. Considerable body of literature exist on these effects [11-13]. Apart from the changes in the DEA process, there are other features inherent to the condensed phase like the inelastic scattering of the electron with other species before it reaches the “target molecule”. More importantly the presence of other species in the immediate neighbourhood may provide a direct channel for secondary chemical reactions of the radicals and ions produced by the electrons. Chemical control may be achieved by controlling the DEA process through changes in the lifetime, energy and the decay channels by appropriate choice of substrate and/or co-adsorbed molecules with the products of the DEA then undergoing further reactions with the neighbouring molecules.

3. **Gas Phase Studies**

3.1. **Control through threshold energies**

![Figure 2. The dissociative attachment cross sections for dominant ions from CS₂. The left extreme shows S⁻, the middle one for CS⁻ and rightmost one for S₂⁻ formation. As discussed in the text, below 4 eV only S⁻ is produced, but at the higher energy resonance at 6 eV all the three types of ions produced. The continuous signal at higher energies is due to the polar dissociation process of the excited neutral molecules (from Ref. 14).](image-url)
Dissociative attachment process is known to show state selectivity from early days of work in this area. As discussed above, this selectivity is due to different bond dissociation energies and the electron affinity of the fragment which eventually carries away the extra electron. Figure 2 illustrates this for the case of CS$_2$ [14]. It is found that all possible fragment ions are formed from CS$_2$ through the DEA process. However, only S$^-$ is formed at the lowest resonance, whereas all the fragment ions are found to be formed at higher energy resonance. In this case, by keeping the electron energy below 4 eV the dissociation is directed to only the S$^- +$ CS channel. There are many other examples of similar behaviour, particularly those involving halogen containing molecules like chloro-flouro methanes. Since the C-F bond dissociation energy is larger than that of C-Cl bond dissociation and the electron affinity of Cl is slightly larger than F, it is found that Cl$^-$ is formed at near zero electron energies, while F$^-$ is formed at electron energies above 2 eV [2, 15, 16]. Such a property has recently been cleverly utilized in complete chemical transformation of a molecular film of 1,2-Cl$_2$F$_3$Br$_2$ (see below). Another example of this is the site selective dissociation of DNA bases by slow electrons (of energy less than 3 eV) in the H abstraction channel of the DEA process [17].

3.2 Control by initial excitation of the molecule
As discussed above vibrational excitation followed by electron attachment has been found to enhance the DEA cross sections by several orders of magnitude [1, 2, 5]. Most of the results indicated an increase of cross sections in the existing channels. However, the DEA to vibrationally excited C$_6$H$_8$BrCl produced by heating, the two competing DEA channels leading to the formation of Cl$^-$ and Br$^-$ were found to have rather anomalous temperature dependence [18] pointing to the possibility of controlling or enhancing specific dissociation channel in a given molecule using a combination of mode selective laser excitation followed by electron collision. There are very few results in this direction, where molecules are prepared in selected states before electron attachment. DEA to electronically excited O$_2$ (\$^3\Delta_g\$) molecules produced in a microwave discharge showed the presence of new resonances that could not be formed from the ground state molecules due to the selection rules [7]. The measurements on electronically excited SO$_2$ molecules formed by UV laser excitation showed that while one of the resonances seen in the ground state attachment gets enhanced in cross section by a factor of six, another resonance gets completely suppressed [19]. Initially the absence of the resonance was explained as due to symmetry based selection rules. However, another set of measurements in which the exciting laser could be tuned through a series of vibronic levels (which are expected to lead to different electronic states through vibronic couplings) showed that the different Franck-Condon region from which electron attachment occurs may be responsible for the absence of the second resonance [20]. These measurements also showed that excitation of vibrational levels above $R_v$ (Fig. 1) may not lead to an increase in the DEA cross sections. As seen in figure 2, the DEA to CS$_2$ molecules in their ground state produces S$_2^-$ in addition to other fragment negative ions. S$_2^-$ can be formed only through a complex dynamics of the negative ion resonance, which breaks two C-S bonds and forms an S-S bond. This entails strong bending mode vibrations in the resonance. Considering this, one expected that the DEA cross section for S$_2^-$ formation from an electronic state of CS$_2$ with bent geometry would show an enhancement. This could be done by exciting the ground state molecules which are in the linear state to the bent excited state using a 308 nm laser. However, the DEA data from such a measurement showed that while the cross sections for S$^-$ and CS$^-$ increased several times, S$_2^-$ was absent beyond detection limits [21]. These results indicate that while electronic excitation dramatically changes the DEA process, detailed measurements are needed for understanding and exploiting this.

3.3 Control through functional group dependence
The chemical properties of all molecules are defined by the functional groups existing in them. Molecules with the same functional groups show very similar optical absorption bands [22]. In the case of electron-molecule collisions, electron transmission spectra indicated the presence of similarity in the formation of resonant attachment in water and its alkyl derivatives [23]. They had also observed
that the electron transmission spectra of benzene derivatives are largely uniform and resemble that of benzene, despite large differences in symmetry [24]. It is also seen that the compilation of data on resonances in aromatic molecules and heterocyclic molecules shows distinctly similar resonance positions in them [25]. More recent electron transmission measurements on selected amino acids showed the presence of almost identical shape resonances arising from the electron attachment to the $\pi$ orbital of the COOH group [26], indicating the functional group dependence in electron attachment. However, the presence of functional group dependence in DEA was brought out only very recently through a set of systematic measurements in various organic molecules [27, 28]. These measurements showed that electron attachment to alcohols, carboxylic acids and amines lead to formation of core excited resonances which fragment to give mostly H$^-$ ions and these resonances could be identified with the resonances seen from H$_2$O, CH$_4$ and NH$_3$ depending on the presence of the O-H, C-H or N-H bonds in the molecules. Measurements on molecules which have H atoms substituted with D atoms at selected sites showed that the resonant behaviour is localized at specific sites for a given electron energy depending on the functional group and the dissociation of the negative ion resonance occurs only at that particular functional group. This was explained as due to both energy and charge localization at a given site following electron capture. That each of the functional group has characteristic electron attachment energy allows using electron energy as a control parameter to selectively break C-H, N-H and O-H bonds in molecules. The distinguishing feature of the functional group dependence is that the site/bond selectivity is not related to the minimum energy requirement for breaking a given bond as discussed in the case of CS$_2$ and the halogen containing molecules. The selectivity occurs in an energy range above 4 eV which is above the threshold energy needed in breaking any of the three bonds under discussion. The site/bond selectivity arising from the functional group dependence has also been observed in bigger molecules like Thymine [29] and higher alcohols [30]. It has also been shown that one can identify the contribution from the methyl group and the aromatic ring in the molecules using methyl substitution at specific sites in the ring [29].

In order to channel the site/bond selective dissociation of molecules into practically useful situations, it is necessary to characterize the state of the radical that is created in the DEA process. One would also like to know if it is a two particle fragmentation or a three particle fragmentation since the kinetic energy of the electron giving rise to the observed site selective fragmentation is fairly high. If it is a two-particle fragmentation, how is the excess energy distributed in terms of the kinetic energy and internal energy of the fragments. These questions were answered by measuring the kinetic energy and angular distribution of the H$^-$ ions using the recently developed Velocity Map Imaging technique [31]. The measurements indicated that the functional group dependence exists even in the angular distribution of the fragments. It showed that the orientation of the particular bond with respect to the incoming electron determines the capture process, rather than the whole molecule [32]. The kinetic energy of H$^-$ shows that for the case of N-H and O-H bonds the dissociation is a two-body process, while that for C-H it is a three-particle break up.

4. Clusters

There are several experiments reporting dissociative electron attachment to clusters. But the one relevant to the present discussion is the well known nucleophilic displacement (S$_N$2) reaction achieved using DEA to molecules in a mixed cluster. The cross section for the production of Cl$^-$ from CH$_3$Cl is seen to be at undetectable limits ($< 10^{-23}$ cm$^2$). However, when this molecule was made into a cluster with NF$_3$ and the cluster was subjected to low energy electron collision, copious signal of Cl$^-$ and Cl$^-$ .CH$_3$Cl could be obtained. The DEA to NF$_3$ molecules is known to produce F$^-$ with very large cross section as a broad resonance centred at the electron energy of 2 eV [33]. These ions after being formed in the cluster react with the CH$_3$Cl molecules within it forming the Cl$^-$ and Cl$^-$ .CH$_3$Cl ions. The electron energy at which these ions are produced is identical to that forming F$^-$ from NF$_3$, confirming the nucleophilic displacement reaction [34]. This study in a cluster indicates that such reactions could be made to take place in condensed phase, probably with far more efficiency providing increased potential for practical applications.
5. Control in condensed phase
While gas phase studies provide information at the single molecule level, it is the condensed phase that is most likely to lead to practical applications of the chemical control by electrons, since the condensed phase provides larger density of one or more species in close proximity which allows the chemical reactions to proceed efficiently. However, it must be said that practical application of electron controlled chemistry already exists in gas phase in the semiconductor industry, though this was empirically arrived at. For example, the optimisation of electron temperature in a fluoroarbon plasmas to produce CF₃ (x = 1 to 3) radicals most efficiently in order to etch the SiO₂ substrates. In the context of condensed phase, efforts are on towards transforming one chemical entity into another, using low energy electrons and towards nanolithography. For example, ozone was synthesized in the condensed phase by electron bombardment of multilayer films of molecular oxygen condensed at temperatures below 30 K on metal surfaces [35] and CO was formed by low energy electron collision on thin films of acetone condensed at low temperature on a solid Ar substrate [36]. Electron induced reactions of cyclopropane in the condensed phase producing propene [37], bond selective dissociation of alkanethiol based self-assembled monolayers adsorbed on gold substrate [38] and oxidation of InP(110) surface through DEA to O₂ condensed on it [39] are further examples. Complete chemical transformation of a film of C₂F₄Cl₂ into C₂Cl₂ using subexcitation electrons through bond selective DEA is an example of chemical control in bulk using electron energy as a control parameter [40]. Partial fluorination of hydrogenated amorphous Si(111) surface by low energy electron irradiation of adsorbed CF₄ [41] and electron induced functionalization of diamond by small organic groups [42] point to possible applications of electron controlled chemistry in nanolithography. As pointed out earlier [41], by choosing adsorbates having appropriate DEA resonances, it may be possible to induce reactions on semiconductor surfaces efficiently in a spatially selective way in nanometre scale by low energy electron irradiation using a Scanning Tunnelling Microscope (STM).

The subject of control in electron induced chemistry will not be complete without referring to the recent and exciting developments at physical and chemical manipulation of isolated single molecules on surfaces using STM. The inelastic collision of tunnelling electrons from the STM tip has been used to break individual bonds [43-45] in molecules. The role of resonant attachment in dissociating the molecules using STM was identified in the case of O₂ [46]. STM was used to induce and control molecular motion surfaces [47-50]. Conversion of a trans-2-butene molecule into a 1,3-butadiene molecule on the Pd(110) surface [51] and dissociation of iodobenzene into iodine atom and phenyl radical followed by joining of two phenyl radicals to form a biphenyl molecule [52, 53] have demonstrated enormous possibilities of chemical control at individual molecule level using STM.

6. Outlook
From the success so far at efforts in using free electrons to control chemical reactions it appears that it is likely to provide practical applications ahead of the more glamorous activity taking place using coherent control and femtosecond lasers. However, there is much to be done both in terms of generating basic data on electron interaction with molecules in gas phase, in clusters and in condensed phase, which could be used for fine tuning various processes leading to practical applications. There is very limited efforts so far in applying the electron based control for a practical application in gas phase, unless one considers plasma as an extension of the gas phase work. Most of the work in plasmas has been empirical in nature. In order to apply the bond selective chemistry in plasmas, it may be necessary to control the electron energy distribution in plasmas to finer ranges than what has been achieved [54-58]. The basic information generated on the interaction of low energy electrons in the gas phase and in the condensed phase along with the use of STM is very likely to bring out new applications of electron controlled chemistry in the near future.

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