Controlling molecular fragmentation using low energy electrons

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Abstract. We show that functional group dependence exists in dissociative attachment of electrons to molecules and this leads to site and bond selectivity in fragmenting organic molecules at the N-H, O-H and C-H sites using electron energy as a control parameter. This phenomenon is investigated further by measuring the momentum distribution of hydride ions using the newly developed ion momentum imaging technique. We find that while the electron attachment at the O-site leads to a two-body fragmentation, attachment at the C-site leads to few-body fragmentation. Several new phenomena like ‘bond orientation dependent electron attachment’ and direct screening of one part of the molecule by another part to the incoming electron are unravelled in the very rich momentum distribution data of the hydride ions that we have obtained at various resonances.

1. Introduction

A wide variety of techniques have been tried for controlling chemical reactions. The most prominent among these are based on the use of lasers as demonstrated in a number of cases [1-5]. Several other ways for chemical control have also been explored like controlling the orientation of the reacting species as they approach each other (stereodynamic control) [6], core electron ionization or excitation using soft x-rays to effect changes in the fragmentation pattern in gas phase [7] and thin films of organic polymers [8] and single molecule engineering using a scanning tunnelling microscope [9].

As compared to all these techniques dissociative electron attachment offers a much simpler means of achieving bond selective chemistry [10]. The dissociative attachment (DA) process occurs through a resonant capture of the electron by a molecule and the unique characteristics of the formation and decay of the resonance give rise to possible control of the dissociation of the molecule. It is well known that electrons play a major role in the chemistry of plasmas. The importance of electron induced processes in variety of applications is also widely known. In addition to these, there has been a resurgent interest in this area in connection with the origin of life in the universe [11], and in the role of low energy electrons in eventual damage of DNA when biological tissue are subjected to high energy radiation [12]. Examples of electron induced chemistry in gaseous clusters [13] and condensed samples [14, 15] have also been reported. In all these processes, the electron creates highly reactive radicals from neutral species through excitation, dissociation, ionization and dissociative attachment.

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In the DA process, an electron of given energy gets attached to a molecule temporarily forming the excited state of the molecular negative ion as shown in figure 1 for a hypothetical diatomic system AB. The attachment occurs in the Franck-Condon region to form the resonant state $AB^-$, which has a repulsive potential energy curve. This state is unstable against electron ejection (autodetachment) as denoted by $\alpha$ since it lies above the neutral state. The width of $AB^-$ represents the finite lifetime of the state against autodetachment. This width is a strong function of the nuclear coordinates and decreases as the inter-nuclear separation increases till the point $R_c$, at which it becomes zero. If the repulsive state survives against autodetachment till $R_c$, it dissociates to give the stable negative ion $B^-$ and the neutral fragment A. The entire process starting from the formation of the resonance and its subsequent dissociation to form a stable negative ion is called dissociative attachment (DA).

![Figure 1. Schematic of the DA process. The arrow $a$ shows the autodetachment process and the arrow $d$ the dissociation process. $R_c$ is the inter-nuclear distance beyond which the negative ion resonance cannot decay through autodetachment and undergoes only dissociation.](image)

The probability for the formation of $B^-$ is a product of the electron capture cross section, $\sigma_c(\varepsilon)$, at energy $\varepsilon$ and the probability $p(\varepsilon)$ that the resonance survives against detachment. Following O’Malley [16] this could be written as

$$\sigma_{DA}(\varepsilon) = \sigma_c(\varepsilon)p(\varepsilon)$$

(1)

where the survival probability

$$p(\varepsilon) = \exp\left(-\int_{R_c}^{R} \frac{\mathcal{I}_a(R)}{hv(R)} dR\right) \cong \exp\left(-\frac{\tau_d}{\tau_a}\right)$$

(2)

with $\mathcal{I}_a$ the autodetachment width, $v(R)$ the velocity of separation of A and $B^-$ and $\tau_a$ and $\tau_d$ are the autodetachment time and dissociation time respectively.

From this equation we could see that the probability for DA changes exponentially with the time taken by the system to cross $R_c$. The strong isotope effect seen in the DA process can be understood from this behaviour. This also explains the large increase in DA cross sections if the neutral molecule is in vibrationally excited state before the electron collision. Several orders of magnitude increase in DA cross sections have been observed in some of the molecules, just by heating them to several hundred degrees Kelvin prior to electron collision [17].

2. Selectivity in DA

The DA process is known to show some degree of selectivity in bond breakage from the early days of work in this area. This is through the threshold energy needed to break a given bond and the electron affinity of the fragment negative ion. The examples for this are many, particularly those involving halogen containing molecules. The recent reports of interest in this respect are the site selective dissociation of DNA bases in the H abstraction channel of the DA process [18] and complete chemical transformation of a molecular film of 1,2-C$_2$F$_4$Cl$_2$ [19] by slow electrons (of energy less than 3 eV). In all these cases the selectivity is achieved through the threshold energy requirement for a particular fragmentation channel. However, the unique dynamics of the DA process resulting from the competition between the autodetachment and dissociation offers far more possibilities for selective fragmentation. These do not depend on the threshold energy needed for breaking a given bond.

2.1. Overcoming IVR

Intra-molecular vibrational energy redistribution (IVR) has been found to be the main stumbling block in using lasers for selective fragmentation of molecules. The question is how much of IVR comes into
play in the DA process. Unlike photoexcitation process, the electron attachment process involves an extra electron. This brings forth qualitative changes as to how the system reacts to the excess available energy. The additional electron brings with itself a new decay channel for the state – the autodetachment process. The lifetime for this process is relatively short. However, for the DA process to take place, the lifetime should be at least of the order of femtoseconds. Due to the coupling between the electronic and nuclear degrees of freedom, the autodetachment lifetime may vary along different nuclear coordinates. Hence some dissociation channels may be preferred over others in a polyatomic molecule depending on the autodetachment lifetime along that particular coordinate. We believe that these naturally built in time controls may limit the IVR in the DA process.

Since the DA process is very sensitive to the initial nuclear coordinates of the neutral molecules, a mode selective vibrational excitation or electronic excitation of a neutral molecule prior to the electron collision could be used to select or enhance a specific dissociation pathway in a polyatomic molecule. Very little effort has gone in this direction due to the inherent difficulties in preparing molecules in specific excited states with enough target densities. Recent experiments on DA to electronically excited SO$_2$ in various vibrational levels in the Clements’ band showed that a particular resonance was suppressed altogether [20]. In DA to electronically excited CS$_2$, it was found that the channel leading to the formation of S$_2^-$ disappears on electronic excitation [21]. In DA to vibrationally excited C$_6$H$_3$BrCl produced by heating, the two competing DA channels leading to the formation of Cl$^-$ and Br$^-$ were found to have rather anomalous temperature dependence [22]. All these experiments point 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. However, our recent measurements on small organic molecules show that site selective fragmentation of molecules using electrons is possible even from their ground states [10].

3. Functional group dependence and site-selective fragmentation

In our experiment [10, 20, 23] the electron beam is produced in pulses of typically 200 ns duration. A small magnetic field of about 50 Gauss helps in collimating and guiding the beam. The electrons are allowed to interact with the molecules, which are in the form of an effusive beam from a capillary array. During the interaction, the entire collision region is free of any electric field. Within about 50 ns after the electron pulse, the ions are swept into the time-of-flight (ToF) mass spectrometer by a pulsed electric field of about 500 V/cm. The flight tube of the ToF mass spectrometer is segmented into four coaxial cylindrical tubes. By applying suitable voltages on these cylinders, they are made to operate as an electrostatic lens that helps in focusing all the ions at the detector. The detector is a channel electron multiplier operated in pulse counting mode. The whole system is optimized to have complete extraction, transmission and detection of all the ions, irrespective of their initial kinetic energies and angular distributions. We lose out on mass resolution in this process. However, the resolution is good enough to separate out all the ions of interest in the present case. The energy resolution of the electron beam is about 0.5 eV. The energy scale is calibrated using O$^-$ from O$_2$.

![Graph](image_url)

**Figure 2.** Hydride ion yield curve from (A) CH$_3$COOH (B) CH$_3$CH$_2$COOH and (C) CH$_3$COOD. In (C) we also show H$^+$ from CH$_3$COOH (+) along with D$^-$ (▲) and H$^+$ (□) from CH$_3$COOD. The lines joining the points are for guiding the eye.
Our measurements on the smallest three carboxylic acids showed H⁻ channel to be the most dominant one. Surprisingly, in all the acids this channel displayed three resonances almost identical in position, as shown in figure 2. This suggested a common electron attachment process in these molecules. Coupled to this was the question about the site from which H⁻ is emerging in these molecules. This was investigated by deuterating these molecules at the carboxyl site and looking at the yields of H⁻ and D⁻ ions as a function of electron energy as shown in figure 2(C). The results clearly show that at the two lower resonances, H⁻ is exclusively produced from the carboxyl site, whereas at the third resonance, the dominant contribution to H⁻ intensity comes from the alkyl site.

A comparison of the acid data with that from other molecules available in literature pointed out the possibility that the above results are the manifestation of a deeper and hence more general behaviour. The DA to CH₄ in the H⁻ channel is observed as a broad peak at 9.2 eV [24], similar to what is observed from the alkyl group of the acids in the present experiment. H⁻ formation from H₂O shows similar resonant structure as seen from the carboxyl part of the acids [17]. Further measurements carried out on H⁻ channel from CH₃OH, C₂H₅OH and n-propyl amine and comparison of these with existing data on CH₃OD [25], and NH₃ [17] showed that functional group dependent DA is a general process and leads to site specific fragmentation of molecules using incident electron energy as a control parameter [10].

The observed functional group dependence could be explained in terms of the formation of 'valence excited' Feshbach resonances with the valence excitations taking place at specific sites. Thus while the electron is being captured, the excess energy is transferred into exciting an orbital electron in the molecule. The resonance will occur only if the excess energy matches with the excitation energy of a particular orbital. Hence each of the resonances corresponds to an excited state of the molecule, but for the electron affinity of the state in question. From this point of view, the observed functional group dependence would be similar to the functional group dependence observed in the optical absorption spectra [26]. The site specificity of the fragmentation process follows from the functional group dependence. The electron is excited from an occupied orbital at a specific site to an unoccupied one at the same site. Correspondingly, the atomic core will have less screening of the nuclear charge, thereby increasing the localization of the incoming electron at the same site. This results in the localization of both the excess energy and the electronic charge. Due to the localization of energy, the fragmentation occurs at the site of valence excitation and the excess charge is carried away by one of the fragments.

The functional group dependence that we have observed so far pertains to C-H, N-H and O-H sites. More experiments are needed to see the extent of this behaviour for other groups. Based on the present results, we are able to use electron energy as a control parameter to selectively break the N-H and O-H bonds in molecules without much damage to other bonds. In the case of C-H bond, the selectivity does not appear as good. It may be pointed out that the site selectivity that we have observed is not connected with the threshold energy requirement of breaking a given bond, examples of which have been pointed out earlier [17-19]. In the present case, the selectivity is seen at energies well above the threshold energies for breaking all types of bonds present in a given molecule. While we have investigated the site selectivity only in small molecules, it is apparent that the rule could be generalized to bigger molecules containing these bonds. The direct evidence for this is reported in measurements on thymine and methylated thymine [27]. Recent measurements on various alcohols have shown similar selectivity for the C-H and O-H bonds both in condensed phase and gas phase [28, 29]. It may also be noted that some earlier condensed phase measurements had indicated possible selectivity [30] which could be explained based on our findings.

4. Probing site selectivity using velocity map imaging
From a practical point of view towards chemical control and from fundamental physics point of view, it is necessary to measure the energy partitioning in these processes like the excess energy that is released as kinetic energy of the fragments and the fraction that is redistributed in terms of their internal energy. In the extreme situation, the H⁻ ejection need not even be two-body break up; it could be a few-body break up depending on the available energy. We address these issues by measuring the
kinetic energies and angular distributions of the H\textsuperscript{-} ions using the newly developed Velocity Map Imaging (VMI) experiment [31, 32].

In the VMI experiment, we employ a similar electron collision set up as described earlier, except for important changes in the ToF spectrometer and the ion detection scheme. A schematic of the experiment is given in figure 3. The ions are produced by the interaction of a pulsed electron beam of about 100 ns duration on an effusive molecular beam formed by a capillary array. They are extracted using a delayed extraction field into the VMI time of flight spectrometer. The ions are detected using a two-dimensional position sensitive detector (PSD) made of three microchannel plates in Z stack configuration and a wedge and strip anode.

![Figure 3. Schematic of the VMI experiment.](image)

The arrival time and position coordinates of each ion are stored separately using a CAMAC based data acquisition system. Because of the cylindrical symmetry of the collision process about the axis of the electron beam, the central slice of the ‘Newton sphere’ containing the electron beam axis provides all the relevant information. This slice is obtained using appropriately narrow time window in the time of flight data as the Newton sphere arrives at the detector. The ion extraction field and the biases on the lens electrode and the flight tube are adjusted to get best imaging. Using this apparatus we could reproduce the well known angular distribution data for various molecules including O\textsuperscript{-} from O\textsubscript{2} [31]. We optimized this further for H\textsuperscript{-} ions using DA to H\textsubscript{2}O [32].

![Figure 4. Velocity map images of the D\textsuperscript{-} ions at the first resonance.](image)

The VMI data for H\textsuperscript{-} and D\textsuperscript{-} ions from partially deuterated acetic acid (CH\textsubscript{3}COOD) and methanol (CH\textsubscript{3}OD) from each of the three resonances were measured. The data at the first resonance are shown in figure 4. These plots are ion signal intensity distribution (shown in the 3\textsuperscript{rd} dimension) in a plane containing the electron beam. The arrows indicate the direction of the electron beam. The radial size of the image represents the magnitude of the velocity of the ions. At this resonance no H\textsuperscript{-} is formed from the C-site and only D\textsuperscript{-} from the O-site is formed. In the figure the D\textsuperscript{-} data from the two molecules are compared with H\textsuperscript{-} from H\textsubscript{2}O. The data on H\textsuperscript{-} from H\textsubscript{2}O show all the features known from previous measurements using conventional techniques [33, 34]. The distribution peaks at about 100\textdegree. Also the
ion kinetic energies represented by the radial distribution) appear to range from zero to a little over 2 eV indicating vibrational excitation of the OH fragment as reported earlier [33, 34]. In comparison, the kinetic energy distributions from CH$_3$COOD and CH$_3$OD are distinctly narrow. This shows that limited energy redistribution is taking place before dissociation. It also indicates a clear two-body fragmentation. The most striking aspect of the VMI data is the distinctly similar angular distribution for acetic acid and water. Even for the case of methanol, the similarity is hard to escape. The angular distribution of D$^-$ from CH$_3$COOD and CH$_3$OD appear to be peaking at about 110°, similar to that for H$^-$ from H$_2$O. The angular distributions of the negative ions are known to be dependent on the symmetry of the neutral molecule and that of the negative ion resonance. It is expected that for molecules of lower symmetry groups, the angular distribution should get correspondingly less anisotropic. However, what we see here is contrary to that. The basic reason for similar angular distribution is that the electron is attaching to the O-H site. However, in order to maintain similar angular distribution, the orientation of the O-H bond with respect to the incoming electron beam has to remain the same, independent of the orientation of the molecule as a whole. Such a phenomenon, which we term ‘bond orientation specific DA’ is observed for the first time.

![Figure 5](image.png)

**Figure 5.** Velocity map images of the hydride ions at the second resonance. (a) D$^-$ from CH$_3$COOD at 7.7eV electron energy (b) D$^-$ from methanol CH$_3$OD at 7.9eV electron energy and (c) H$^-$ from H$_2$O at 8.5eV.

The VMI data on the hydride ions at the second resonance in CH$_3$COOD and CH$_3$OD are shown in figure 5 along with that from H$_2$O. The data from acetic acid and methanol appear to be fairly similar. However they are quite different from that seen from water. The kinetic energies and the angular distribution clearly show a two body fragmentation mechanism in both the acid and the alcohol molecules. There is also a clear forward – backward asymmetry in the angular distributions.

In all these velocity map images, a small but significant ‘hole’ is observed in the forward direction within a small angular range. The fact that this observation is not an artifact of the imaging system can be verified by comparing with data from water at the second resonance as shown in figure 5(c). This sharp feature can be understood considering the two-body nature of the dissociation process as well as the O-H site specific contribution to the hydride ion signal. As we have shown earlier, at these resonances, the hydride ion comes from the O-H site. For two-body type dissociation, neglecting the rotational motion of the molecule, the electron must approach the O-H site from the side opposite to the hydrogen in order to give hydride ions in the forward direction. A sharp decrement in the hydride ion signal in the forward direction clearly indicates that the electrons are not reaching the site within appropriate angular range. This could happen only if the remaining part of the molecule shadowing the O-H site from the incoming electrons.

Considering the resonance position on the energy scale, the corresponding de-Broglie wavelength of the electrons is of the order of 4Å, which is much more than the actual bond lengths of these molecules but not as big compared to the electronic orbital sizes. The site selective nature of the process i.e. the involvement of highly localized molecular orbitals gives this unique effect, which is observed for the first time in any scattering experiment. In fact, the observation of this ‘shadow’ effect is a clear indication of the electron beam not exactly behaving like a plane wave near the molecule.

At the third resonance, the hydride ions are formed from both the O-H and C-H sites leading to the formation of both H$^-$ and D$^-$ from the CH$_3$COOD and CH$_3$OD molecules as shown in figure 6.
However, the differences in the VMI of H⁻ and D⁻ are very striking in each of these molecules. In general it appears that H⁻ ions are formed with relatively less kinetic energy as compared to D⁻. Also D⁻ ions have specific angular distributions. This clearly indicates that this resonance is composed of two different electron capture processes; one at the C-site and the second one at the O-site. We also note that angular distributions of D⁻ are different from each other in the two molecules. While acetic acid shows a distribution more like the second resonance in water (figure 5(c)), methanol seems to have a distribution peaking strongly in the backward direction. At the third resonance in methanol, scrambling of the hydrogen atoms has been observed earlier [35]. We are unable to see the presence of scrambling in the hydride ion channel. However, the more or less isotropic distribution underlying the strong backward distribution of D⁻ in methanol poses interesting questions about the dynamics of the DA process. We also note that the ‘hole’ seen in the forward direction at the first two resonances, is present at the third resonance also for the case of acetic acid, but is absent for methanol.

![Figure 6. Velocity map images of the hydride ions at the third resonance. (a) H⁻ and (b) D⁻ from CH₃COOD at 9.1 eV and (c) H⁻ and (d) D⁻ from CH₃OD at 10.1 eV.](image)

It appears that the H⁻ ions are formed with relatively very little kinetic energy in the case of methanol. This points to a few-body fragmentation process. For acetic acid also the H⁻ ions have less kinetic energy, but larger than that of methanol. However, we notice a totally unexpected right-left (90° – 270°) asymmetry with respect to the electron beam. One expects complete cylindrical symmetry about the electron beam direction. The only way this symmetry could be broken is through a preferential molecular orientation. We use a 50 Gauss magnetic field in our experiment for collimating the electron beam. On reversing the magnetic field we find that the right-left asymmetry is still maintained, but in the opposite way. We believe that the asymmetry may be resulting from a sequential fragmentation process with the intermediate molecular ion oriented in a specific way due to the presence of the magnetic field. This ion on further dissociation may give rise to H⁻ with the observed angular distribution. We are unable to comment further on this. Reverting to the kinetic energy distribution of H⁻, it appears that the electron attachment at the C-site leaves the molecule with more than one fragment, clearly indicating the larger scale damage that electron attachment at the C-site does. This may be of great significance in the radiation induced damages in biological tissues.

5. Summary
We have shown that functional group dependence exist in the DA process in the hydroxyl, methyl and amine groups. This is explained in terms of the formation of valence excited Feshbach resonances at the O-H, C-H and N-H sites respectively. Since electron attachment to each of these sites occur at distinctly different energies, electron energy can be used as a control parameter to selectively break bonds in organic molecules. This site selectivity is not connected with the threshold energy requirement of breaking a given bond. The selectivity is seen at energies well above the threshold energies for breaking all types of bonds present in a given molecule. Momentum imaging of the hydride ions resulting from the O-H and C-H sites in methanol and acetic acid using the newly developed velocity map imaging technique provides unprecedented details of the fragmentation dynamics of the resonances. While the electron attachment at the O-site leads to a two-body fragmentation, attachment at the C-site leads to few-body fragmentation. New phenomena like ‘bond
orientation dependent electron attachment’ and direct screening of one part of the molecule by another part to the incident electron are unraveled in the very rich momentum distribution of the hydride ions.

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