Probing site selective fragmentation of molecules containing hydroxyl group using Velocity Slice Imaging

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Abstract. Site selective fragmentation is observed at the hydrogen site in small organic molecules like simple carboxylic acids and alcohols in the dissociative attachment (DA) process. We have investigated this site selectivity in the acetic acid and methanol molecules by measuring the kinetic energy and angular distribution of the hydride ions using Velocity Slice Imaging (VSI) technique. The results are explained in terms of the formation of valence excited Feshbach resonances. The kinetic energy and angular distribution measurements also reveal the dynamics associated with the process.

1. Introduction

A wide variety of activities have been directed towards controlling chemical reactions. Excitation of molecules to specific vibrational levels is one of the approaches [1-6], which target an ensemble of molecules using lasers. Single molecule engineering using inelastic tunneling electrons in scanning tunneling microscopes has been used in a number of cases to break individual bonds [7-9] and to induce as well as control molecular motion on surfaces [10-14]. Soft X-rays has also been used in the context of controlling unimolecular reactions in polyatomic species [15] and in selective bond scission by site-specific core excitation using soft x-rays on thin films of organic polymers [16].

Low energy electron collision on molecules resulting in dissociative attachment (DA) is another technique that could lead to site selective fragmentation of molecules. The simplest way this could be achieved is using the threshold energy dependence for breaking different bonds in a given molecule. It has been demonstrated in the site-selective dissociation of DNA bases by slow electrons (of energy less than 3 eV) in the H-abstraction channel [17]. The complete chemical transformation of a molecular film of 1, 2-C2F4Cl2, again using electrons of energy less than 3 eV [18] is another example of this approach. However, the unique dynamics of the DA process offers far more possibilities of selective fragmentation of molecules beyond the threshold energy dependence.

In the DA process, the dissociation of the resonant state is in competition with the decay through autodetachment. In order to have reasonable “survival probability” the autodetachment time should be of the order of vibrational time scales. However, the two modes of decay are also interdependent through the strong coupling between the nuclear and electronic degrees of freedom. A mode selective vibrational excitation or electronic excitation of the neutral molecule prior to the electron collision could thus be used in a polyatomic molecule to select or enhance a specific dissociation pathway [19-21]. These experiments point to the possibility of controlling or enhancing specific dissociation
pathways in a given molecule by a combination of mode selective laser excitation followed by \( DA \)
with free electrons or even the quasi-free Rydberg electrons. However, recently we have demonstrated
the site selective fragmentation of molecules in the case of the hydride ion production from the \( DA \) to
simple organic molecules [22]. The electron energies at which this site selectivity is observed is
beyond the threshold energies for the hydride ion formation from all these sites. In order to understand
the molecular dynamics that leads to this site selectivity, we carried out the kinetic energy and angular
distribution measurements of the hydride ions formed in \( DA \) to compounds containing hydroxyl group
namely acetic acid and methanol.

We have investigated the dynamics behind this site specificity by measuring the angular
distribution and kinetic energy of the hydride ions using Velocity Slice Imaging (\( VSI \)) technique [23,
24], which we developed for low energy electron collision experiments. In the case of diatomic
molecules, under the assumption that the molecule does not rotate within the time scale of \( DA \), the
angular distribution of the fragment anion will directly indicate the preference for a particular
orientation in the form of anisotropy in differential cross section. Knowing the initial state of the
neutral molecule and this anisotropy one can determine the symmetry of the negative ion state
involved in the \( DA \) process. Similarly in the case of polyatomic molecules, if the dissociation process
is a simple two body break up, the angular distribution of anion will indicate the dependence of the \( DA \)
cross section with the orientation of the bond that is broken with respect to the electron beam [25, 26].
In that case the fragment anion angular distribution will also provide the information about the
negative ion state that is addressed in the \( DA \) process.

The information on the kinetic energy that is proportional to the square of the radius of the \( VSI \)
of the fragment ion reveals the energetics of the \( DA \) process. Hence measurement of angular distribution
along with the kinetic energy of the anion fragment can provide in-depth information about the
dynamics of the \( DA \) process such as the energy partitioning, possible many-body break-ups,
rearrangement before dissociation if any, symmetry and dissociation limits of the resonances accessed
etc. The information about the energy distribution so obtained will also be useful in understanding the
internal state of the neutral fragment in the case of two body break ups. This information is essential in
realizing the potential of this approach towards controlling the chemical reactions using electrons
involving these species of molecules.

2. Experimental
The velocity slice imaging set-up that is used in these experiments, is described in details elsewhere
[23, 24]. In short, the set-up consists of a pair of electrodes, namely pusher and puller, flanking the
interaction region. The puller electrode is followed by another electrode called lens electrode, which is
followed by the 50mm long flight tube. A set of three micro-channel plates (\( MCP \)) arranged in \( Z \)-stack
configuration along with wedge and strip anode is used as the position sensitive detector (\( PSD \)). A
pulsed electron beam and a delayed ion extraction using a pulsed electric field are used in the
experiment. This arrangement helps in applying sufficiently strong ion extraction field without
affecting the low energy electron beam and in providing the necessary blooming of the Newton sphere
of ions for velocity slice imaging. The pulsed operation also helps in measuring the flight time of the
ions. One modification we made in the present experiment over the previous reports [23, 24] was to
fix a fine wire mesh on the puller electrode. This was necessary while working with the hydride ions.
Because of their relatively larger velocities, they bloom into a larger sphere before they are extracted.
It was found that larger electric fields had to be employed for maintaining the velocity map imaging
condition for the fast moving hydride ions. The wire mesh prevented the field penetration from the
lens and flight tube into the interaction region. The performance of the \( VSI \) set-up is found to be
satisfactory by comparing the angular distributions obtained for hydride ion from water with that
reported in the literature. The arrival time of each ion at the detector along with the position
information is stored separately using the ‘list’ mode data acquisition. The delayed extraction provided
appropriate time spread for ‘time sliced’ velocity imaging. The central time sliced image of the
‘Newton sphere’ of ions was obtained by selecting appropriate time window during analysis of the list
mode data. This time sliced image corresponds to the ions ejected in the plane parallel to the detector and containing the electron beam axis. It provides the necessary information on the velocity distribution of the ions.

The pulsed electron beam is obtained from a simple electron gun based on thermionic emission and is collimated using a pair of magnet coils situated outside the vacuum chamber. Typical electron beam pulse width is about 150nsec. The negative ions generated are extracted using a pulsed electric field after a delay of about 100nsec. The effusive molecular beam is generated using a capillary array. The molecular beam is made to pass in the direction of the PSD along the axis of the VSI set-up and made to cross the electron beam at right angle at the center of the interaction region.

In order to identify the hydride ions from different sites within a given molecule, partially deuterated acetic acid (CH₃COOD) and methanol (CH₃OD) are used. Hence, the H⁻ signal obtained in the DA process is directly correlated with the dissociation at the C-H site whereas the D⁻ signal corresponds to the O-H (O-D) site.

3. Results and discussions

The ion yield curves (relative intensity as a function of electron energy) of H⁻ ions from undeuterated acetic acid along with the H⁻ and D⁻ signal obtained from partially deuterated acetic acid are shown in figure 1. The data show three resonances in hydride ion channel at 6.7eV, 7.7eV and 9.1eV. As can be seen from the signal from partially deuterated sample the first two resonances are clearly corresponding to the O-H site of the molecule whereas the third resonance is predominantly coming from the C-H site with little contribution from the O-H site.

![Figure 1. H⁻ and D⁻ ion yield curves from CH₃COOH and CH₃COOD: (+) H⁻ from CH₃COOH, (▲) D⁻ from CH₃COOD, (□) H⁻ from CH₃COOD. The lines joining the points are for guiding the eye.](image)

Similarly, in the case of methanol three resonances are observed in the hydride ion channel at 6.4eV, 7.9eV and 10.1eV. The measurements on CH₃OD have shown that the H⁻ peak, observed at 10.2 eV, originates from the C site, whereas the peaks at 6.4 eV and 7.9 eV originate from the O site [27].

3.1. First resonance

We have obtained the velocity slice images of the D⁻ from CH₃COOD and CH₃OD at the first resonance (6.7eV and 6.4eV respectively) and compared them with the velocity slice image obtained for the hydride ions from the water molecule at its first resonance (at 6.5eV). The three images are shown in figure 2. The striking similarity between the angular distribution of the hydride ions from the OH site of all three molecules indicate the very basic feature of the origin of this resonance, which is associated with the presence of oxygen site.
Figure 2. Comparison of VSI of hydride ions at first resonance from (a) acetic acid (6.7 eV) and (b) methanol (6.4eV) and (c) water (6.5 eV).

The acetic acid molecule belongs to $C_s$ symmetry group. The ground state of acetic acid is $1^1A'$.
From the angular distribution that peaks at 100° i.e. close to 90°, the information about the negative ion state can be retrieved. Using the selection rules for the electron capture process in the polyatomic molecule of $C_s$ symmetry it can be shown that the angular distribution that is observed for the first resonance corresponds to the $A' \rightarrow A'$ type of transition [26]. The recent experimental and theoretical studies on the excited states of acetic acid show a valence transition in its absorption spectrum around 7 eV that corresponds to the excitation of valence electron to the $14a'$ orbital [28]. This orbital is known to be highly localized on the O-H bond in the molecule. This explains the site selective fragmentation that occurs at the O-H site in the acetic acid at this energy. This implies that this resonance is a characteristic one to the hydroxyl group explaining the functional group dependent nature of the site selectivity.

From the angular distribution of the $D^-$ ions from methanol it can be concluded that this resonance corresponds to the $A' \rightarrow A'$ type of transition [26]. However in the absence of theoretical calculations of the molecular orbitals of the neutral excited states of methanol, nothing much can be said about the molecular orbital picture of the resonance.

It is interesting to note that there exists a distinct similarity in the angular distribution pattern of the hydride ions from acetic acid as well as from methanol at the first resonance and that from water at the resonance situated at 6.5 eV as can be seen from figure 2. Assuming that the $DA$ process is localized to the bond that is broken and the molecule does not undergo substantial rotation in the dissociation timescale (which is of the order of vibrational time scale), the anisotropy in the angular distribution in a specific ion yield points out the preference to a specific orientation of the bond that is broken towards electron capture. Hence we conclude that the resonance leading to this fragmentation channel is very specific to the hydroxyl group and will occur in all compounds that contain this group.

The kinetic energy of the $D^-$ ion from acetic acid at the first resonance is determined from the radii of the angular distribution obtained in VSI. The appearance energy (threshold) for getting hydride ion from the O-H part of the acetic acid molecule through $DA$ can be estimated from the bond dissociation energy of $D(CH_3COO-H) = 4.77$ eV [29, 30] and the electron affinity for H (0.75 eV) [31]. The appearance energy for H$^-$ is calculated to be 4.02 eV. The threshold associated with the formation of $D^-$ ion from CH$_3$COOD can be assumed to be the same as that for H$^-$ from the O-H part in the CH$_3$COOH molecule. It is seen that the kinetic energy varies from 0 to 2.9 eV with maximum at around 1.2 eV. It may be noted that the energy distribution will have the electron energy spread convoluted into it.

The most probable kinetic energy distribution for hydride ions from this resonance is found to be 1.2 eV and the known threshold for $D^-$ formation is 4 eV. This implies that 1.5 eV of energy seems to
have been left as internal excitation of the neutral fragment for the electron energy of 6.7 eV. This can be
in the form of vibrational or electronic excitation of that fragment. The possibility of the three-
body break-up is ruled out as the excess energy is relatively small. Moreover, a three-body
fragmentation is expected to give isotropic angular distribution, which is not the case here.

In the case of methanol the kinetic energy of $D^-$ ion is found to be in the range 0 to 2.4 eV. The
distribution is found to be narrower than the one from acetic acid. At the resonance, the kinetic energy
distribution is found to be peaking at about 1.2 eV. The energy threshold for getting the $D^-$ ion from
the O-D site in methanol can be determined using the electron affinity of D atom (0.75 eV) and the
bond dissociation energy for (CH$_3$O-H) (4.5 eV). The bond dissociation energy of the CH$_3$O-H bond is
found from the thermochemical data available. The enthalpy of formation of CH$_3$O radical ($\Delta H_f$
(CH$_3$O) = 17 kJ/mol) [32], the enthalpy of formation of H atom ($\Delta H_f$ (H) = 218 kJ/mol) [33] and the
enthalpy of formation of CH$_3$OH molecule ($\Delta H_f$ (CH$_3$OH) = -201 kJ/mol) [34] gives the
corresponding bond dissociation energy to be 436 kJ/mol giving the value of threshold energy for H$^-$
from CH$_3$O-H through $DA$ to be 3.75 eV. The threshold for $D^-$ from CH$_3$O-D is expected to be very
much close to that value.

From the energy threshold for this channel and from the electron energy as well as the most
probable value of the kinetic energy of the hydride ion it is clear that about 1.4 eV energy has gone
into the internal excitation of the remaining neutral fragment. This may appear as the vibrational or
electronic excitation of that fragment. The anisotropy observed in the angular distribution of the $D^-$
ions rules out the three body break-up of the system in the $DA$ process.

3.2. Second resonance

The angular distribution for the $D^-$ ions taken at the second resonance is shown in figure 3. The
angular distribution clearly shows the anisotropy, which is indicative of two-body break-up.

![Figure 3. VSI of $D^-$ ion from (a) CH3COOD and (b) CH3OD at second resonance](image)

In the case of acetic acid it is also found that the $D^-$ ion energy is in the range 0 to 3 eV. At 7.7 eV
the peak in the kinetic energy distribution is at 2 eV. Since the appearance energy for $D^-$ is 4 eV, this
corresponds to an internal energy of 1.7 eV in the neutral fragment. A comparison of this with that of
the first resonance shows that the most probable internal energy of the neutral fragment is almost the
same (1.5 eV vs 1.7eV) at both the resonances. This indicates that both the resonant states may have
the same dissociation limits as far as the O-D bond breakage is concerned considering the two-body
break up mechanism.

In the case of methanol it is found that the energy distribution extends up to about 3.5 eV and peaks
at about 1.5 eV. Since the appearance energy is 3.75 eV, we may conclude that on average there is
about 2.7 eV of energy going into the internal excitation of the remaining neutral fragment. This is
considerably higher than the corresponding partitioning of energy into the neutral fragment at the first
resonance, which is about 1.4 eV. It is not clear how the 2.7 eV is being distributed into internal
modes of the neutral fragment. However, the possibility exists that the second resonance in methanol could have a different dissociation limit as compared to that of the first resonance.

3.3. Third resonance

At the third resonance, the hydride ion signal comprises of predominantly H⁻ signal along with a very weak D⁻ signal. The VSI's of both H⁻ and D⁻ signals from 9.1 eV resonance for acetic acid are shown in figure 4. The angular distribution for the D⁻ signal clearly shows anisotropy with cross section peaking at 90°. The VSI of H⁻ shows a dominant central structure surrounded by a pattern similar to that of D⁻ seen at the same energy. We identify the weak intensity distribution on the outside as due to small amount of impurity in the form of CH₃COOH present in the sample.

![Figure 4. VSI of (a) D⁻ and (b) H⁻ from CH₃COOD at third resonance.](image)

For D⁻ the energy seems to range from 0 to 4.5 eV peaking at 1.9 eV. This indicates that the remaining neutral fragment carries considerable amount of energy as its internal excitation (about 3.2 eV). From the anisotropy seen in the angular distribution, one may conclude that the dissociation is still a two-body process, though considerable internal energy is left in the neutral fragment. Based on the energy partitioning it is safe to conclude that the resonance that leads to this DA channel has a different dissociation limit than that for the first two resonances.

In the case of H⁻ ions the kinetic energy distribution has fairly large intensity at zero eV and extends up to 4 eV. As noted above in this case there is a contribution due to H⁻ formed from the O-H part of the CH₃COOH present in the sample, which would be identical to the D⁻ kinetic energy distribution. Thus the kinetic energy distribution corresponding to the C-H bond break is the one that shows very little most probable value. This value is found to be about 1 eV.

In order to determine the energy partitioning into the neutral fragment, it is required to know the appearance energy of H⁻ from the C-H part of acetic acid. We calculate it as follows. The appearance energy (threshold) for getting the hydride ion from the carbon site (C-H part of the molecule) for formic acid can be estimated from the available thermochemical data. The enthalpy of formation of COOH⁻ i.e. \( \Delta H_f(\text{COOH}^-) = 597 \pm 8 \text{ KJ/mol} \) [34] and the ionization energy of COOH is 791 kJ/mol [36]. Hence \( \Delta H_f(\text{COOH}) \) becomes −194 kJ/mol. Knowing the \( \Delta H_f(H) = 218 \text{ kJ/mol} \) [34], \( \Delta H_f(\text{HCOOH}) = -378.6 \text{ KJ/mol} \) and electron affinity of H (EA (H) = 0.75 eV) [34] the appearance energy for H⁻ is found to be 3.43 eV. As the acetic acid is not structurally much different from the formic acid, except with the hydrogen atom at the carbonyl part, which is replaced by a methyl group, the threshold energy for the formation of H⁻ from CH₃COOH can be approximated to be close to 3.43 eV (The threshold for obtaining H⁻ from CH₄ through DA is estimated to be 3.78 eV).

Based on the appearance energy of 3.4 eV and the most probable kinetic energy of H⁻ measured as 1 eV, the energy deposited in the neutral fragment is 4.7 eV. This energy should be sufficient to cause
further dissociation. Thus the low kinetic energy and relatively isotropic angular distribution observed in the H\(^-\) channel show the possibility of a three-body break up at this resonance.

The VSI for both the ions at this resonance in the case of methanol is shown in Figure 5. The D\(^-\) shows highly anisotropic angular distribution with a forward backward asymmetry while that for the H\(^-\) is isotropic. The kinetic energy distribution is found to be within the range of 0 to 2 eV in the case of D\(^-\) ions. This distribution peaks at 0.8 eV with a narrow width. As the appearance energy for the D\(^-\) ions from the O-D site is about 3.75 eV, it is clear that the energy gone into the internal excitation of the remaining neutral fragment is about 5.5 eV, which is indicative of its electronic excitation. Also anisotropy present in the angular distribution indicates the two-body break-up, at least in the time scale of the D\(^-\) ejection. The large internal energy left in the neutral fragment indicates that the negative ion resonance state involved in the D\(^-\) formation process has different dissociation limit as compared to the previously discussed resonance states.

![Figure 5. VSI of (a) D\(^-\) and (b) H\(^-\) from methanol at third resonance](image)

The threshold energy for the H\(^-\) formation on electron attachment to CH\(_3\)OD is 3.5 eV (\(\Delta H_f\) (CH\(_2\)OH) = -9 kJ/mol [32], \(\Delta H_f\) (CH\(_3\)OH) = -201 kJ/mol [34], \(\Delta H_f\) (H) = 218 kJ/mol [33] and E.A. (H) = 0.75 eV [34]). Our data show the H\(^-\) ions the kinetic energy distribution to be in the range of 0 to 3 eV peaking at 0.5 eV. Thus the excess energy remaining in the neutral fragment in this case is about 6 eV, which is quite large. The kinetic energy distribution peaking close to zero energy and the isotropic angular distribution indicate that the H\(^-\) formation is taking place through at least a three-body break up.

It is clear from the VSI obtained for both H\(^-\) and D\(^-\) ions from CH\(_3\)COOD and CH\(_3\)OD molecules at different resonances that negative ion resonance states that are involved are with different symmetries as well as different dissociation limits. As can be seen from the absorption spectra of these molecules [28, 35] there are many neutral electronic transitions that exist in the relevant energy range. The rich absorption spectra of these molecules in this energy range indicate valence and Rydberg transitions overlapping with each other. Hence it is difficult to assign a particular neutral excited state as the parent state for the negative ion that plays role in the DA process at given electron energy.

To conclude, we have studied the dynamics of the process that leads to the site selectivity in the fragmentation of acetic acid and methanol in DA. The results obtained clearly indicate the role of valence excited resonances in these processes. The kinetic energy information and the nature of dissociation like two- body break up and many body break-up may be important in modelling the observed DA to DNA bases [36, 37]. It is also observed that the maximum damage to DNA through low energy electron attachment via single and double strand breaks happens at around 10eV. This energy range corresponds to the C-H bond break in simple organic molecules. Our identification of the three-body break up at the C-H bond in the DA process may explain the relatively large damage seen at around 10 eV in the electron induced damage to DNA [38].
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