Functional Group Dependent Site Specific Fragmentation of Molecules by Low Energy Electrons

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Functional group dependence is observed in the dissociative electron attachment (DEA) to various organic molecules in which the DEA features seen in the precursor molecules of the groups are retained in the bigger molecules. This functional group dependence is seen to lead to site-selective fragmentation of these molecules at the hydrogen sites. The results are explained in terms of the formation of core-excited Feshbach resonances. The results point to a simple way of controlling chemical reactions as well as interpreting the DEA data from bigger biological molecules.

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Control of chemical reactions has been a long cherished dream towards which a variety of approaches have been taken. The most prominent approach toward this has been the use of lasers. For molecular collisions, control has been achieved by mode-selective excitation [1–3] or by stereodynamic control and by control of orbital alignment [4]. In the case of unimolecular reactions, control has been achieved by quantum interference between different reaction pathways connecting the same initial and final states and by adjusting the temporal shape and spectral content of ultrashort chirped laser pulses [5–7]. While these efforts target an ensemble of molecules, single molecule engineering using inelastic tunneling of electrons in scanning tunneling microscopes has been used to break individual bonds [8–10] and to induce as well as control molecular motion on the surface [11–14].

Soft x rays have also been used in the context of controlling unimolecular reactions in polyatomic species. Excitation of the C 1*s* electrons in acetone were found to affect the fragmentation pattern depending on whether the 1*s* electron gets ionized or excited into a Rydberg-like orbital or into an antibonding π^* molecular orbital with the fragmentation occurring around the site of the carbon atom where the optical excitation took place [15]. Active control of chemical bond scission by site-specific core excitation using soft x rays on thin films of organic polymers was also demonstrated recently [16].

Low energy electron collision on molecules resulting in dissociative attachment 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 as demonstrated in the site-selective dissociation of DNA bases by slow electrons (of energy less than 3 eV) in the H-abstraction channel of the dissociation of the negative ion resonance [17] and complete chemical transformation of a molecular film of 1, 2-$C_2F_4Cl_2$, again using electrons of energy less than 3 eV [18]. However, the unique dynamics of the dissociative electron attachment (DEA) process offers far more possibilities of selective fragmentation of molecules beyond the threshold energy dependence, which have not been realized till now.

In the DEA 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. This dependence has been highlighted by the observed isotope effect and the large increase in the DEA cross sections in heated target gas molecules [19,20] and selectively prepared excited vibrational levels [21] prior to electron collisions. 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. Our recent experiments on DEA to laser excited molecules show that electronic excitation of the molecules prevent the appearance of the DEA signal in a particular resonance altogether [22] or suppress a particular dissociation channel [23]. In another experiment of the DEA to vibrationally excited C_6H_4BrCl produced by heating, the two competing DEA channels leading to the formation of Cl^- and Br^- were found to have rather anomalous temperature dependence [24]. 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 DEA with free electrons or even the quasi-free Rydberg electrons. In this Letter we report our observation of a novel process of functional group dependence in the DEA process leading to site-selective fragmentation of molecules and the possibility of using electron energy as a parameter for control of chemical reactions.

In the present experiments, an effusive molecular beam was allowed to interact with a magnetically collimated and pulsed electron beam under single collision conditions [25,26]. Typical energy resolution of the electron beam was 0.5 eV. The negative ions formed in the interaction region were extracted using a fairly high pulsed electric field (typical pulse height $\sim$200 V/cm and duration

5 μ sec.) delayed with respect to the electron pulse by about 100 nsec. The ions were mass analyzed using a segmented time-of-flight (TOF) spectrometer and detected using channel electron multiplier operated in the pulse counting mode. The combination of the pulsed high field extraction and the segmented TOF mass-spectrometer ensured complete collection and detection of all the ions produced in the interaction region irrespective of their initial kinetic energies and angular distributions [25,26].

The measurements were carried out on small carboxylic acids, alcohols, and an amine. Dissociative electron attachment experiments on the small carboxylic acids have been reported earlier [27–30]. Though these experiments show negative ions of almost all the possible fragments, they did not show the formation of H^- ions. In contrast, the experiments carried out by us on formic acid [26] and present measurements on acetic acid and propionic acid show H^- formation as one of the dominant channels in DEA to these acids. The failure to detect H^- in the earlier measurements may be attributed to its small mass. Being the lightest, H^- ions take away most of the excess energy of the dissociation process conserving energy and momentum. Consequently, special efforts are needed to collect, mass analyze, and detect them.

The ion yield curves (relative intensity as a function of electron energy) of H^- ions from the acetic acid and propionic acid are shown in Fig. 1. The data show three resonances in each of the acids. Though there appears to be a difference in the peak intensities, their positions are at almost identical energies indicating very similar behavior for the DEA process. In order to investigate the reason for this striking similarity, we carried out measurements on partially deuterated acetic acid (CH_3COOD). In this case we find that both H^- and D^- ions are produced, but at different electron energies. The resulting ion yield curves of H^- and D^- are shown in Fig. 2. We note that H^- appears as a broad peak at an energy corresponding to the third peak seen from undeuterated acetic acid. Being a broad peak, its tail overlaps with second peak from the undeuterated acid, but the first peak is clearly absent. Whereas the D^- ion yield curve shows that the ions are produced predominantly at the first two resonances.

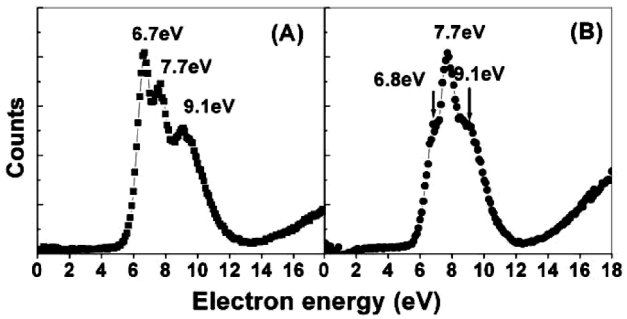

FIG. 1. H^- ion yield curve from (a) acetic acid and (b) propanoic acid.

Measurements on partly deuterated propionic acid also show a similar behavior. These results taken together clearly indicate that the methyl group and the carboxyl group in these molecules retain their separate identity in the DEA process leading to H^- formation and that a given group behaves in a similar way almost independent of the rest of the molecule.

That these results are the manifestation of a deeper and hence more general behavior could be concluded from a comparison of the existing data on several molecules and further measurements that we carried out. To begin with, the DEA behavior seen in a functional group should be seen in its parent molecule. For example, the resonance identified from the methyl group should correspond to a resonance in methane in the same electron energy range. We note that the dissociative attachment in CH_4 in the H^- channel is observed as a broad peak, similar to what is observed from the methyl group in the present experiment centered at 9.2 eV [31]. There also appears to be further evidence that the methyl group property is retained in the DEA in acetic acid from the presence of a resonant peak in the CH_2^- channel at almost the same energy in both molecules (10.4 eV in acetic acid as compared to 10.3 eV in CH_4) [31]. We also note that H^- formation from H_2O by DEA shows similar resonant structure as seen from the carboxyl part of the acids. DEA with water gives rise to H^- formation at 6.5 eV and 8.6 eV respectively [19]. The first excited state of water lies at 6.67 eV above the ground state and the 6.5 eV resonance has been identified as a core-excited Feshbach resonance [32]. We believe that the observed resonant attachment at the carboxyl site of the acid may correspond to this resonance in H_2O. It is also likely that the 7.7 eV resonance from the carboxyl group in the acids may correspond to the 8.6 eV resonance in H_2O, with the difference in energy being due to influence of the neighborhood atoms. If the similarity between the carboxyl group and H_2O is indeed valid, a corresponding similarity should exist among alcohols, the carboxylic acids, and H_2O.

This was confirmed by our measurements on CH_3OH and C_2H_5OH. As given in Fig. 3, the H^- yield in these two

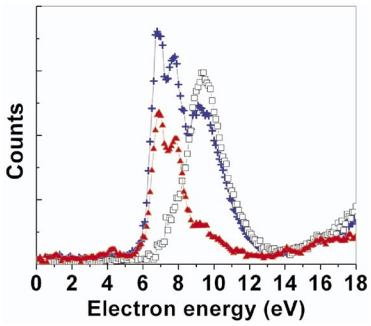

FIG. 2 (color online). H^- and D^- ion yield curves from CH_3COOH and CH_3COOD: (+) H^- from CH_3COOH, (▲) D^- from CH_3COOD, (□) H^- from CH_3COOD. The lines joining the points are for guiding the eye.

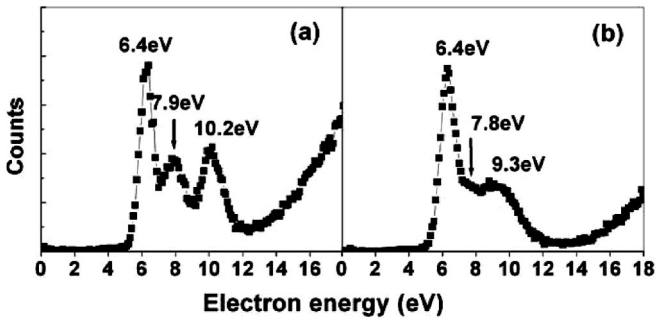

FIG. 3. Ion yield curves of H^- from (a) CH_3OH and (b) C_2H_5OH.

molecules shows three resonances, very similar to what is seen in the carboxylic acids. The first two resonances appear at 6.3 and 7.9 eV, respectively, analogous to that seen from H_2O and the third one appears to be similar to that one seen from corresponding alkane. We also note that measurements on CH_3OD have shown that the H^- peak observed at 10.2 eV originates from the C site, whereas the peaks at 6.3 eV and 7.9 eV originate from the O site [33]. This adds further support to our observation of a functional group dependent DEA in molecules and the site-specific fragmentation of molecules using incident electron energy as a control parameter.

We explored the functional group dependence in the DEA process further by studying an amine. In Fig. 4 we give the ion yield curve for H^- from *n*-propyl amine which shows a strong peak at 5.2 eV and a smaller but broader peak at 8.8 eV. The first peak could be clearly assigned to the amine radical, as DEA to NH_3 is known to give a strong peak at 5.7 eV in the H^- channel [19]. The second peak at higher energy is expected to be a mixture of H^- from the amine group as well as the propyl part of the molecule.

Theoretical calculations of the DEA process even in simple diatomic molecules are difficult and successful attempts in examining this process satisfactorily in polyatomic molecules are just emerging [32,34]. However, the observed functional group dependent DEA can be explained qualitatively. The H^- formation in the cases we discussed arises from the core-excited resonances. This

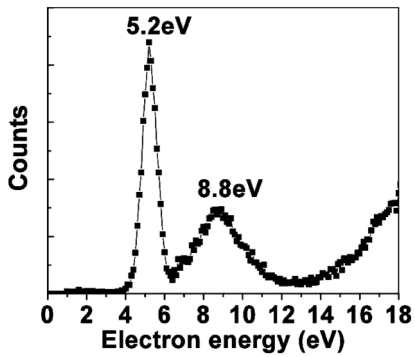

FIG. 4. Ion yield curve of H^- from *n*-propyl amine.

implies the excitation of an electron from a specific orbital to a higher orbital while the incoming electron is captured by the molecule. These excitations appear to occur depending on the functional groups in molecules, as seen from their absorption spectra [35]. Hence the electron will be excited from a fairly localized orbital. Once this electron is excited, the corresponding atomic core will have less screening of the nuclear charge. Subsequently the incoming electron is likely be localized in the vicinity of this atom. This results in the localization of both the excess energy and the electronic charge. Since the DEA occur in vibrational time scales, there will be relatively little energy redistribution. Because of the localization of energy, the fragmentation occurs at the site of core excitation and the excess charge is carried away by one of the fragments.

There are two questions related to the specificity of the observed process. Are there other channels of dissociation at the resonances that we have observed and how general is the observed phenomenon? Though the second question could be answered only by having actual measurements in other molecules, some clues to the answers could be obtained by looking at the type of core excitations in the molecules concerned. The lowest bands in the absorption spectra of H_2O, NH_3, and CH_4 are known to have Rydberg type excitation [35]. The absorption spectra of the amines and the alcohols are also known to have similar types of excitation as those for their precursor molecules [35]. However, in reality the Rydberg configuration is known to have strong configurational mixing with the conjugate valence shell configuration, the best example being H_2O. The Rydberg orbital is delocalized and nonbonding in character whereas the excited valence shell maintains the localization and is antibonding in nature in these molecules. The resonances formed by the Rydberg excitation thus will have a larger lifetime against dissociation, giving enough time to have structural changes in the molecule with possible scrambling of the atoms [36]. In such a situation the resonance could decay through more than one channel as seen in the case of H_2O and CH_3OH where anions other than H^- are formed at the resonances discussed here. The relative intensities of these channels will depend on the autodetachment rate as a function of the nuclear coordinates as well as the speed with which a particular dissociation process will occur. The abstraction of H or H^- is likely to be dominant in this situation based on the velocity of the fragmentation process. On the other hand, the valence shell excitation due to its strong antibonding nature will lead to very quick dissociation with a specific bond being broken with few other possible channels. In the case of CH_3OH, the first two resonances produce only H^- and CH_3O^- whereas the third one leads to the formation of O^- also. It has also been seen that at the third resonance the hydrogen atom scrambling occurs [33,37] indicating a larger lifetime against dissociation for this state. This is consistent with a Rydberg-like nature of the excited state seen in the absorption spectrum. It may be noted that even at this resonance, the cross section for

the formation of H^- is larger than that for the formation of O^-. In the case of acids, the resonances observed could be identified with a Rydberg, valence and another Rydberg, respectively, based on the absorption spectra [35]. However, the first Rydberg state has a strong overlap with its conjugate valence state. The strong site specificity observed in the first two resonances may thus be related to the valence nature of the excitation, whereas the less specificity seen in the third resonance could be attributed to the Rydberg nature of the excited state. Thus it appears that core-excited resonances with valence shell excitation may lead to more site specificity in the fragmentation channel.

To conclude, we have shown that H^- formation due to DEA from small organic molecules follows a pattern depending on the specific group or atom to which the hydrogen is attached. This pattern is similar to that seen from the parent molecule of the group. More importantly, by tuning the electron energy to the respective resonant energy we are able to selectively break the molecule at different locations. This functional group dependence of the DEA may explain the similarity of features observed in DEA to DNA bases [38]. It may be possible to generalize our findings to bigger molecules [39] as well as to the molecules in a condensed phase [40] and also help in modeling the electron induced damage to DNA [41]. The H^- formation from the hydrophilic or hydrophobic sites within a given molecule as a function of electron energy could have important implications in analytical techniques and, most importantly, in modifying and controlling chemical reactions.

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