

## FUNCTIONAL GROUP DEPENDENT SITE ELECTIVE FRAGMENTATION OF SIMPLE ORGANIC MOLECULES USING LOW ENERGY ELECTRONS

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Controlling the molecular dynamics has been considered to be one of the most effective ways to control the chemical reactions. There have been several ideas proposed in this direction that include the mode selective chemistry [1], and quantum interference of the various product channels leading to enhancement or suppression of a particular product channel [2]. With the advent of lasers these ideas were realized in actual experiments. The idea of mode selective chemistry has been demonstrated in a number of cases in reactive collisions involving molecules and in channel selective photo-dissociation of molecules [3]. Inelastic tunneling of electrons in a scanning tunneling microscope has also been used in a number of cases to break individual bonds and induce and control molecular motion on surfaces [4]. In our recent experiments we find that collision of free electrons to small organic molecules could be used to selectively fragment the molecules at specific sites using electron energy as a control parameter through the dissociative electron attachment process. We find that this selectivity is not due to specific energy thresholds as has been reported for some cases till now [5], but due to the core excited nature of the resonances.

In our studies of dissociative electron attachment (DEA) to some simple organic molecules like simple carboxylic acids, alcohols and an amine, some specific patterns in the resonant structure for the  $H^-$  channel are observed. These patterns are found to be specific to the functional groups associated with the molecules and in turn similar to the pattern shown by the precursor molecule of the functional group. For example, in the case of acetic acid ( $CH_3COOH$ ), the prominent resonances are observed in the  $H^-$  channel at 6.7 eV, 7.7 eV and 9.1 eV. The study of DEA to partially deuterated acetic acid ( $CH_3COOD$ ) revealed that the first two resonances are associated with the breaking of O-H bond. The corresponding energies are found to be close to the resonances observed for the same channel in DEA to the water molecule. The third resonance is found

to be coming from the C-H bond breaking and energetically close to that observed for ethane. We also observed similar behavior in the alcohols. The  $H^-$  ion yield curve from the amine also provided results as expected from  $NH_3$ , thus conforming the functional group dependent selective fragmentation in the DEA process.

We explain our observations qualitatively in terms of core excited resonances. The core excitation by the incoming electron is similar to the case of photo-absorption in which a particular orbital electron is excited. The absorption spectra of molecules with same functional groups show remarkable similarity [6]. Once this electron is excited, the corresponding atomic core will have less screening of the nuclear charge. Subsequently the incoming electron is likely to 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 occurs in vibrational time scales, there will be relatively little energy redistribution. Due to 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.

### References

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