

## Probing functional group dependence in dissociative electron attachment using negative ion momentum imaging

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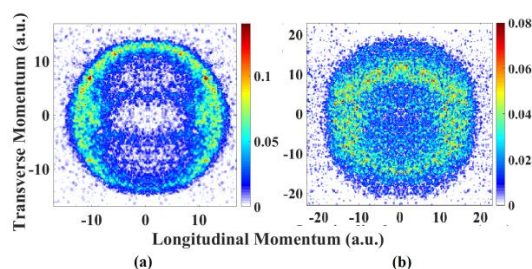
**Synopsis** Dissociative electron attachment (DEA) is the most efficient way to explore the structure and dynamics of excited states of molecular negative ions. More importantly, DEA has been shown to be a tool for chemical control. One crucial aspect of the chemical control using DEA is the functional group dependence present in this process. Here we present cases on the effect of delocalized electrons on DEA patterns observed in simple aromatic compounds.

It has been shown that  $H^-$  formation from DEA to aliphatic compounds follows a pattern that depends on the functional group present and roughly mimics that shown by the prototype hydride - e.g.  $H^-$  from DEA to alcohols and amines show parallels with that from DEA to water and ammonia, respectively [1]. This functional group dependence of DEA process leads to site selective fragmentation of N-H, C-H and O-H bonds using electron energy as a control parameter. Beyond 4eV of electron energy, this site selectivity has been found to stem from core excited resonances. In the case of N-H and O-H bonds, the localization of excitation is understood to be due to lone pair excitation of N or O atom. As noted above, prior studies of functional group dependent site selectivity have been largely restricted to aliphatic compounds [1]. However, in aromatic organic molecules like aniline, benzyl amine, pyrrole, delocalized electrons influence this site selectivity due to mixing of lone pair electrons.

In pyridine, where lone pair electrons of N do not become part of delocalized pi electron cloud,  $H^-$  from C-H site shows exactly same DEA behaviour as that from benzene [2]. On the other hand, in aniline,  $H^-$  from its N-H site shows deviation in DEA dynamics as compared to that from ammonia because of influence lone pair electrons. Whereas in benzyl amine, as lone pair electrons are shifting away from delocalized pi electron cloud,  $H^-$  from N-H site shows simi-

lar DEA behavior as that from ammonia at same electron energy [3].

Pyrrole is a five membered heteroatomic aromatic compound in which lone pair electrons of N become part of delocalized pi electron cloud.  $H^-$  from its N-H site (Figure 1(a)) shows similar angular distribution as that from aniline.  $H^-$  from its C-H site (Figure 1(b)) shows intriguing dynamics unlike that from benzene. We believe that this distinguishing feature might be a signature of mixing of lone pair electrons with delocalized pi electron cloud. We also compare pyrrole results with N-methyl pyrrole under similar conditions.



**Figure 1.**  $H^-$  momentum images at (a) 5.5 eV and (b) 9.5 eV from DEA to pyrrole.

### References

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