

Study of Fragmentation Dynamics of Polyatomic Molecules

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This dissertation concerns the study of fragmentation dynamics of polyatomic molecular ions created by soft x-ray photons or energetic charged particles such as electron or heavy ion impact on neutral molecules. We pay particular attention to the rare process of associative fragmentation, i.e. the formation of a bond between atoms that are separated in the neutral molecule, but get associated during the evolution of the neutral molecule into an unstable molecular ion. Investigation of migration of atoms and bond formation between the atoms in the molecular ion during fragmentation using the multi-ion coincidence momentum imaging technique is the focus of the thesis.

We studied the formation of H_2^+ and S_2^+ ions formation from the dissociative ionization of H_2O and CS_2 molecules. Formation of these associative ions suggests that geometrical deformation of molecular ion probably activates the association reaction. This idea is extended to polyatomic molecules. We have initially chosen the symmetric tetrahedral CH_4 molecule for investigation of intra-molecular association between hydrogen atoms. We have observed the formation of H_2^+ ion from singly and doubly ionized CH_4 molecule. The association reaction would be altered if we replaced any one H atom by another atom, especially by a highly electronegative atom or radical. Hence, we have investigated the *atom substitution effect* on the H–H association reaction in CH_4 molecule. This is done by changing over to molecules such as CH_3Cl and CH_3OH and observing the association of H atoms. In addition to the formation of H_2^+ , H_3^+ is found from dissociative ionization of CH_3Cl and CH_3OH , which was not observed in CH_4 . In fact, the presence of the $-Cl$ radical enhances triple association (H_3^+) even more than pair association (H_2^+). This implies that deviation from tetrahedral symmetry in $CH_3Cl_2^+$ is large and brings the three H atoms very close to each other.

The role of chemical group (methyl and hydroxyl groups) in bond association is investigated in the CH_3OH molecule. To distinguish between the H atom of hydroxyl group or methyl group, we have used the isotope tagging method. Substituting the H atoms in methyl group by D atoms (i.e. performing the experiment with CD_3OH instead of CH_3OH), we are able to identify whether a certain reaction channel involves the hydroxyl or the methyl group. This enables investigation of *site-specific atom-atom association*. We found that the formation probability of H_3^+ and H_2^+ from methyl group alone is five times more than the formation of same ions from both group of H atom migration and association. In summary, we have explored various aspects of associative reactions in fragmentation dynamics of polyatomic molecular ion using momentum imaging technique. The association reaction may depend on various factors such as the perturbation, geometry of molecule, electronegative sites in molecule, etc. Our comparative study of associative reactions in various molecules indicates that the deformed geometry of precursor ion plays a key role for enhancing the associative ion formation. Further, we have found some signatures of the role of functional groups in a molecule in the kinetic energy distributions of the associative ions. We have been able to show that the momentum maps offer a way of estimating the geometry of the precursor molecular ion under certain conditions, namely when a three body break-up of a doubly or triply charged precursor ion occurs. In case where there is only one neutral fragment, its kinetic energy can be determined from the momentum balance in the reaction, thus enabling an analysis of the kinetic energy release in the reaction. Modelling of the trajectories of fragments under Coulomb repulsion and comparison of the trajectories with the observed fragment momenta under simple models and assumptions has enabled us to estimate some of the geometrical parameters of the precursor molecular ions.

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