

Attosecond Charge Migration in Non-covalently Bonded Clusters

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Abstract

In general, charge migration can occur via pure electron-electron correlation and relaxation or via coupling with nuclear motion. We must understand both aspects of charge migration through the noncovalent bond to harness full potential of the non-covalently bonded clusters. In my poster presentation, I have focused on the pure relaxation- and correlation-driven charge migration, subsequent charge localization and finally on charge directed reactivity in the noncovalent bonded clusters. Pure relaxation- and correlation-driven charge migration can occur in several hundred attosecond time scale and this is why chemical dynamics associated with this pure electronic charge migration can be named as "Attochemistry". One of the efficient ways to elucidate the Attochemistry is via the vertical ionization by monitoring a non-stationary electronic charge density which evolves in time while the nuclear configuration remains unchanged. So far, Attochemistry of several halogen, chalcogen, pnictogen, and tetrel bonded clusters has been studied theoretically by our group. In my poster I shall present different aspects of charge migration e.g. electron correlation, inter-nuclear distance, driving force of charge migration, vibrational and rotational effect and charge directed reactivity. To probe such kind of pure correlation driven charge migration I shall show that high harmonic generation (HHG) spectroscopy will be useful. Construction of the HHG beamline and spectrometer will be presented. By using HHG spectroscopy, I shall show how fingerprint of attosecond charge migration can be found. Furthermore, I shall present the numerical simulation of HHG spectrum by solving the 1D-time dependent Schrödinger equation.

Introduction:

Sankhabrata Chandra obtained his B.Sc. degree from St. Xavier's College in 2013. Then he has joined with Dr. Atanu Bhattacharya as an integrated Ph.D. student at Indian Institute of Science. Currently he has submitted his PhD thesis and he is waiting for his thesis defense.

In the context of supramolecular chemistry, crystal engineering and molecular electronics, the hydrogen bond (in which hydrogen atoms act as electrophiles) is one of the most recognized noncovalent bonds; however, researchers are increasingly finding importance of another noncovalent bond: the halogen bond (in which halogen atoms can act as electrophiles).¹³ Halogen bonding has recently

been found to be one of the most interesting noncovalent interactions for constructing many photosensitive organic materials. In general, an intermolecular noncovalent bond $A-X\cdots B$, can typically be represented by positioning two molecules such that the X atom of one molecule, A-X, acts as a bridge to an atom B of another donor (lone pair of electrons) molecule. The noncovalent bonds are named after the nature of the X atom. When the hydrogen atom takes the place of X in the bridging position, it is called the hydrogen bond.¹⁹ Similarly, when a halogen atom (e.g., Cl) takes the place of the X atom in the bridging position, it is called halogen bond.¹³

Recently, halogen bonding has been the subject of immense scientific interest for constructing supramolecular assemblies.¹ According to the IUPAC recommendation, "a halogen bond occurs when there is evidence of a net attractive interaction between an electrophilic region related to a halogen atom during a molecular entity and a nucleophilic region in another, or an equivalent, molecular entity."² Therefore, from a simplistic point of view, an intermolecular halogen bond, $AX\cdots B$, is formed when two molecules are positioned such that the halogen atom (featured by X) of the electron acceptor molecule (A-X) acts as a bridge to an atom B of another electron donor molecule. In the same configuration, when hydrogen atom takes the place of X in the bridging position, the $AH\cdots B$ is called the hydrogen bond which is the most conceived noncovalent bond.

Discussion and Conclusion:

Here we demonstrate, compare and contrast relaxation- and correlation-driven charge migration dynamics in halogen, chalcogen, pnictogen and tetrel bonded clusters, following their vertical ionization. For this work, we have selected different isolated $A-X:NH_3$ clusters, where A represents F, Cl, CN and NH_2 substituents and X features Cl, SH, PH_2 and SiH_3 to exhibit specific noncovalent bonding interaction. The charge migration dynamics in these clusters is studied using the density functional theory (DFT) with the $wB97XD$ functional and the $6-31+G(d,p)$ basis set. Approximately 400-600 attosecond duration is predicted for charge migration in (1: 1) $AX:NH_3$ complexes. Effects of basis set and intermolecular distance on the ultrafast charge migration dynamics through the halogen, chalcogen, pnictogen, and tetrel bonded clusters also are discussed. This is the primary report on pure relaxation- and correlation-driven charge migration dynamics in chalcogen, pnictogen and tetrel bonded clusters.

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In the case of the hydrogen bond, A and B atoms are more electronegative than H atom, and as a result, partially positively charged-H atom is attracted to the lone electron pair(s) of B.³ In addition, a certain amount of charge is transferred from the B lone pair into a σ^* anti-bonding A-H orbital, which weakens and lengthens the A-H covalent bond. In the case of halogen bond, on the other hand, the bridging halogen atom does not possess a partial positive charge, like the hydrogen bond. Instead, due to highly anisotropic electrostatic potential of the bridging halogen atom, it contains a ring of negative charge that surrounds a crown of positive charge extended along the A-X bond, which is often referred to as a σ hole.⁴ This σ hole region is attracted to the partial negative charge of the halogen bond acceptor atom B. Similar to the hydrogen bond, there is also a transfer of charge from B atom (usually its lone pair) into σ^* A-X anti-bonding orbital in halogen bond.