



# On the ultrafast charge migration dynamics in isolated ionized halogen, chalcogen, pnictogen, and tetrel bonded clusters



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## ABSTRACT

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<sub>3</sub> clusters, where A represents F, Cl, CN and NH<sub>2</sub> substituents and X features Cl, SH, PH<sub>2</sub> and SiH<sub>3</sub> 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 time scale is predicted for charge migration in (1:1) AX:NH<sub>3</sub> complexes. Effects of basis set and intermolecular distance on the ultrafast charge migration dynamics through the halogen, chalcogen, pnictogen, and tetrel bonded clusters are also discussed. This is the first report on pure relaxation- and correlation-driven charge migration dynamics in chalcogen, pnictogen and tetrel bonded clusters.

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## 1. Introduction

Noncovalent bonds have been the subject of fundamental investigation for many years. Often, from a simplistic point of view, intermolecular noncovalent bonds are described using the notation A–X···B, where two molecules (AX and B) are positioned such that the X atom of the electron acceptor molecule, AX, acts as a bridge to the atom B of the electron donor molecule. The respective noncovalent bond is named after the nature of the X atom. When hydrogen atom takes the place of X in the bridging position, it is called hydrogen bond [1], which is one of the most recognized and carefully analyzed noncovalent bonds. However, researchers are increasingly finding the importance of other noncovalent bonds, formed even without hydrogen atom in the bridging position. They include the halogen bond [2] (in which, a halogen atom, e.g., Cl, takes the place of the bridging X atom), the chalcogen bond [3] (in which X represents one of the chalcogen atoms, e.g., S), the pnictogen bond [4] (where X belongs to the pnictide family of elements, e.g., P) and the tetrel bond [5] (where X is replaced by one of the tetrel atoms, e.g., Si). This definition acknowledges the qualitative structural analogy among halogen, chalcogen, pnictogen and tetrel noncovalent bonding interactions. Unique bonding features

of these non-hydrogen noncovalent bonds are discussed in plethora of recent and old literature because they are found to exhibit important role in supramolecular chemistry, crystal engineering and molecular electronics [2–5]. Although complete electronic and spectroscopic characterization of the halogen, chalcogen, pnictogen, and tetrel bonds still remains an active and attractive area of fundamental physical chemistry research, the aim of the present work is at studying pure electronic aspect of charge migration dynamics in these noncovalent bonded clusters.

For a long time, charge migration phenomenon through hydrogen bonds has been the subject of fundamental investigation [6–10] because charge migration through hydrogen bonds are found to play an important role in biological electron transport [6–8] and molecular conductance [9,10]. After the realization of other noncovalent bonds, such as halogen, chalcogen, pnictogen and tetrel, researchers are also finding (or predicting) the important and significant role of charge migration through these unusual noncovalent bonds in supramolecular chemistry, crystal engineering and molecular electronics [11–14]. For example, bromoaromatic aldehyde-based organic crystals, which feature strong intermolecular halogen bonding contact between the monomer units, exhibit bright green phosphorescence via electronic coupling and charge transfer through halogen bond between adjacent monomeric units [11a]. It is believed that halogen bonding contact promotes charge migration through the halogen bond, which ultimately prevents nonradiative decay path and which, in turn,

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facilities singlet–triplet conversion. Halogen bonding is also found to induce formation of halopentafluorobenzene-based liquid crystal, which is an important material for the construction of optically nonlinear system [11c], in which charge migration through halogen bonds may play an important role. Source of strong chalcogen bonding interaction [12] is connected to a charge transfer through this noncovalent bond. Similarly, energy associated with charge (electron) transfer process is predicted to contribute to pnictogen bonding energy dominantly [13]. Furthermore, charge redistribution as a result of tetrel bond formation is proposed to be an initial step of the  $S_N2$  reaction [14]. These limited, yet profound, recent examples (studies) show that charge migration (or transfer) through the halogen, chalcogen, pnictogen and tetrel noncovalent bonds is ubiquitous. However, all aspects of charge migration through these non-hydrogen noncovalent bonds currently remain poorly-understood, which clearly highlights the need of a fundamental study of charge migration phenomenon through these non-covalent bonds.

Charge migration is a complex process, which often involves the coupling between nuclear and electronic motions; however, recent theoretical works [15–17] show that an interesting charge migration can occur in several hundred attosecond time scale, which can be driven purely by the electron–electron correlation and relaxation. As no nuclear rearrangement is needed to initiate a relaxation- and correlation-driven charge migration, it features pure electronic aspect of charge migration phenomenon. In order to harness the full potential of halogen-, chalcogen-, pnictogen- and tetrel-bonded functional photosensitive supramolecular materials, in which charge migration through these noncovalent bonds is ubiquitous, pure electronic aspect of charge migration phenomenon through these bonds must be well-understood. Furthermore, pure electronic aspect of charge migration, in general, is of paramount interest for physical chemistry community as emerging attosecond spectroscopy, in principle, can experimentally probe this hitherto-unexplored aspect of charge migration phenomenon [19].

Recent literature demonstrates that one of the efficient ways to initiate pure correlation- and relaxation-driven charge migration is via vertical ionization of a molecule or a molecular cluster [15–17]. Recently, we have explored relaxation- and correlation-driven charge migration dynamics through the  $Cl \cdots N$  halogen bond, adopting this vertical ionization scheme, for different  $A-Cl$  ( $A$  represents  $F$ ,  $OH$ ,  $CN$ ,  $NH_2$ ,  $CF_3$  and  $COOH$  substituents) electron acceptor molecules paired with a  $NH_3$  donor molecule [20]. The vertical ionization, which was manifested in our earlier work by removal of an electron from the highest occupied molecular orbital (HOMO), creates a hole in the electron cloud of these complexes. Upon removal of an electron from the HOMO of  $NCCl \cdots NH_3$  complex, the hole is predicted to migrate from the  $NH_3$ -end to the  $Cl$ -end of the complex in approximately 600 attosecond. Other halogen bonded complexes, such as  $H_2NCl:NH_3$ ,  $F_3CCl:NH_3$  and  $HOCCl:NH_3$ , exhibit similar charge migration following vertical ionization. On the contrary,  $FCl:NH_3$  and  $HOCl:NH_3$  complexes do not exhibit any charge migration following removal of an electron from the respective HOMO, pointing to interesting halogen bond strength-dependent charge migration, which is driven purely by electron–electron correlation and relaxation.

Continuing with the same theme, in the present work, we have focused on hitherto-unexplored electron–electron correlation- and relaxation-driven charge migration dynamics in chalcogen, pnictogen and tetrel bonded isolated clusters. The aim of the present work is at comparing and contrasting the influence of substituents and strength of correlation interaction on the electron–electron correlation- and relaxation-driven charge migration dynamics in halogen, chalcogen, pnictogen and tetrel bonded isolated clusters. To address this, we have selected one  $A-X$  molecule paired with one  $NH_3$  molecule (referred as  $AX:NH_3$ ). Here,  $A$  represents  $F$ ,  $Cl$ ,

$CN$  and  $NH_2$  substituents, and  $X$  features  $Cl$  (for halogen bonded clusters),  $S$  (for chalcogen bonded clusters),  $P$  (for pnictogen bonded clusters) and  $Si$  (for tetrel bonded clusters) atoms.

## 2. Theoretical method

Here, vertical ionization scheme is adopted in order to explore different facets of pure electron–electron correlation- and relaxation-driven ultrafast charge migration dynamics in halogen, chalcogen, pnictogen and tetrel bonded clusters. The process of vertical ionization represents removal of an electron from a molecule (or molecular cluster) and therefore, it exhibits creation of a “hole” in the electronic cloud. The subsequent charge migration dynamics triggered by the vertical ionization manifests time-evolution of the created hole. Recent theoretical works show that charge migration dynamics triggered by vertical ionization may take place before the nuclear dynamics starts to play a role [18]. Therefore, for the present work, we have considered the frozen frame nuclei at the vertical ion point and have solved the dynamical Schrödinger equation for the electronic wave function.

In the case of vertical ionization, recently, it has been shown that the density functional theory (DFT) yields results at moderate computational cost for the quantum mechanical treatment of fixed-nuclei-electron dynamics if appropriate DFT functional, which is free from self-interaction error and which includes long range electron–electron interactions, is employed [21]. Therefore, for the present work, we have used two DFT functionals [22], including  $wB97XD$  and  $CAM-B3LYP$ , to explore the charge migration dynamics in halogen, chalcogen, pnictogen and tetrel bonded clusters. Further justification for the selection of these DFT-functionals is given in our previous work [20]. In brief, previously a number of self-interaction-free DFT functionals (such as,  $CAM-B3LYP$ ,  $wB97XD$  and  $M06HF$ ), which are also corrected for long range electron–electron interactions, were compared and contrasted for the study of charge migration dynamics following the vertical ionization of halogen bonded clusters. The complete active space self-consistent field (CASSCF) theory, which uses a restricted active space for building the determinantal expansions of the electronic states and thus satisfactorily introduces static electron–electron correlation in the description of charge migration, was also used and the CASSCF-results were compared with the DFT-results. Furthermore, additional dynamical electron–electron correlation was also incorporated by using complete active space perturbation (CASMP2) theory. We found that the DFT along with the  $wB97XD$  functional predicts results almost similar to the other levels of theory mentioned above.

The 6-31+G(d,p) basis set is used for all calculations (justification of using this basis set is also presented in our previous work) [20]. All geometry optimizations and ionization energy calculations are executed using the Gaussian 09 package [23]. In the present work we have also employed MP2 level of theory to explore geometry and binding energy of the clusters and subsequently we have compared the MP2-result with the DFT-results. Stability of each complex is tested by analyzing the energetic minima and analytical frequencies. The binding energy is calculated as the difference between the sum of monomer energies and the complex (cluster) energy; in which, each monomer unit was optimized separately. For the correction of interaction energy from the inherent basis set superposition error (BSSE), a counterpoise method is used for all complexes [24]. Stability of DFT-wave function is tested using the scheme adopted by Bauernschmitt et al. [25]. The theory of “atoms in molecules (AIM)” [26] has been used to analyze the topology of all the optimized complexes with the help of AIMAll program [27]. The presence of a bond critical point (BCP) and the bond path between  $X$  and  $B$  atoms in the  $X$  non-covalent bond is

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