On the ultrafast charge migration and subsequent charge directed reactivity in Cl⋯N halogen-bonded clusters following vertical ionization

Sankhabrata Chandra, Ganga Periyasamy, and Atanu Bhattacharya

Citation: The Journal of Chemical Physics 142, 244309 (2015); doi: 10.1063/1.4922843
View online: http://dx.doi.org/10.1063/1.4922843
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/142/24?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Ab initio study of the structure, bonding, vibrational spectra, and energetics of X BS + (where X = H , F, and Cl)

The evolution of the monoelectron dihydrogen bond H ⋯e⋯ H in the symmetric and asymmetric cluster anions ( FH ) n(e)( HF ) m

A theoretical prediction on intermolecular monoelectron dihydrogen bond H ⋯e⋯ H in the cluster anion ( FH ) 2 (e)( HF ) 2


The 19 F– 1 H coupling constants transmitted through covalent, hydrogen bond, and van der Waals interactions
On the ultrafast charge migration and subsequent charge directed reactivity in Cl•••N halogen-bonded clusters following vertical ionization

Sankhabrata Chandra, Ganga Periyasamy, and Atanu Bhattacharya

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, India
Department of Chemistry, Central College Campus, Bangalore University, Bangalore, India

(Received 13 March 2015; accepted 9 June 2015; published online 26 June 2015)

In this article, we have presented ultrafast charge transfer dynamics through halogen bonds following vertical ionization of representative halogen bonded clusters. Subsequent hole directed reactivity of the radical cations of halogen bonded clusters is also discussed. Furthermore, we have examined effect of the halogen bond strength on the electron-electron correlation- and relaxation-driven charge migration in halogen bonded complexes. For this study, we have selected A-Cl (A represents F, OH, CN, NH₂, CF₃, and COOH substituents) molecules paired with NH₃ (referred as ACl:NH₃ complex): these complexes exhibit halogen bonds. To the best of our knowledge, this is the first report on purely electron correlation- and relaxation-driven ultrafast (attosecond) charge migration dynamics through halogen bonds. Both density functional theory and complete active space self-consistent field theory with 6-31+G(d,p) basis set are employed for this work. Upon vertical ionization of NCCI:···NH₃ complex, the hole is predicted to migrate from the NH₃-end to the CICN-end of the NCCI:···NH₃ complex in approximately 0.5 fs on the D₀ cationic surface. This hole migration leads to structural rearrangement of the halogen bonded complex, yielding hydrogen bonding interaction stronger than the halogen bonding interaction on the same cationic surface. Other halogen bonded complexes, such as H₃NCl:NH₃, F₃CCl:NH₃, and HOOCCl:NH₃, exhibit similar charge migration following vertical ionization. On the contrary, FCl:NH₃ and HOCl:NH₃ complexes do not exhibit any charge migration following vertical ionization to the D₀ cation state, pointing to interesting halogen bond strength-dependent charge migration. © 2015 AIP Publishing LLC.

I. INTRODUCTION

Charge migration (or transfer) through noncovalent bonds is crucial to a variety of chemical processes. For example, well-known noncovalent interactions, such as hydrogen bonding and van der Waals contacts, have ubiquitous role in biological electron transport. Charge migration along the non-covalently bonded stacks of aromatic cores plays an important role in various organic devices, such as field effect transistors and photovoltaic cells. Molecular conductance is also found to depend on the strength of noncovalent bonds. Therefore, understanding the charge migration dynamics through noncovalent bonds is of both fundamental and practical significance.

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). Halogen bonding has recently been found to be one of the most interesting noncovalent interactions for constructing many photosensitive organic materials. For example, Bolton et al. have recently shown that 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. All aspects of charge transfer through halogen bonds, however, still remain poorly understood, which clearly highlights the need of a fundamental study of charge migration phenomenon through halogen bonds, in general.

Charge transfer is a complex process, which often involves the coupling between nuclear and electronic motions, as well as coupling to the environment; however, recent theoretical and experimental works show that an interesting charge migration can occur in several hundred attosecond time scale, which can be driven purely by the correlated electrons. Therefore, in a broader perspective, charge migration phenomenon exhibits two chemical physics aspects: (1) purely electronic mechanism which is driven only by electron-electron correlation and relaxation, and (2) coupled electron-nuclear mechanism which involves nuclear motion along with the charge migration. The first mechanism can be initiated immediately following vertical ionization of a molecule or molecular cluster and that is why it features purely electronic aspects of charge migration dynamics. In this work, we have focused on investigating this purely electronic aspect of charge migration dynamics through halogen bonds following vertical ionization of representative halogen bonded clusters. Subsequent charge (hole)-directed reactivity of the radical cations of halogen bonded clusters is also discussed to find the connection between specific charge localization and nascent...
radical cationic reactivity. Pure electronic aspects of charge migration are also of another interest for the chemical physics community as emerging attosecond spectroscopy, in principle, can experimentally probe hitherto-unexplored charge migration which does not involve nuclear motion. To the best of our knowledge, there are some reports in the literature that deal with the ab initio investigation of the ultrafast charge transfer through hydrogen bonds following ionization of respective hydrogen bonded clusters; however, the same through halogen bonds following ionization of halogen bonded clusters has not been studied, thus far, constituting a knowledge gap in the field.

To address purely electronic aspects of charge migration through halogen bonds in the representative halogen bonded clusters and their subsequent induced reactivity, we have selected A-Cl molecules paired with NH$_3$ (referred as ACI:NH$_3$ complex in the proceeding presentation). Here, A represents F, OH, CN, NH$_2$, CF$_3$, and COOH substituents. Our selection of these complexes is done based on the fact that the halogen bonds, created by some of these complexes, have been elaborately discussed in the recent literature.

In general, an intermolecular noncovalent bond A-X···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. Similarly, when a halogen atom (e.g., Cl) takes the place of the X atom in the bridging position, it is called halogen bond. Although complete electronic and spectroscopic characterization of the halogen bonds still remains an active area of research, the aim of the present work is to study purely electronic aspects of charge transfer dynamics through halogen bonds following vertical ionization of the ACI:NH$_3$ complexes (where A includes F, OH, CN, NH$_2$, CF$_3$, and COOH). Furthermore, the charge directed reactivity of the nascent radical cations of A-Cl:NH$_3$ systems is also explored in the present work.

II. THEORETICAL METHOD AND BACKGROUND

The process of ionization represents the removal of an electron from the molecule (or molecular cluster) and therefore, it exhibits creation of a “hole” in the electronic cloud. The subsequent electron dynamics triggered by the ionization manifest the time-evolution of the created hole. In the case of a spatial localization of the initial hole, these dynamics can even represent a migration of the hole throughout the system. Recent theory predicts that such migration of a hole can occur on the time scale of attoseconds and can be driven purely by electron correlation and relaxation, which can precede any nuclear rearrangement. This phenomenon can be distinguished from the standard electron (or hole) transfer, which is often discussed in the context of Marcus theory and which is driven by the nuclear motion (hence occurs on much slower time scale).

As long as we are interested in describing processes that take place before the nuclear dynamics start to play a role, one may consider the frozen frame nuclei at the vertical ion point and solve the dynamical Schrödinger equation for the many-body electronic wave function. In the case of ionization, recently, it has been shown that the density functional theory (DFT) yields reasonably accurate results at moderate computational cost for the quantum mechanical treatment of fixed-nuclei-electron dynamics. In this method, the cationic states are approximated by Kohn-Sham (KS) orbitals resulting from solving the cationic KS-DFT equations. It is argued in the recent literature that the KS-DFT method using conventional exchange-correlation functional (such as B3LYP), however, may fail to describe correctly the electron dynamics following ionization due to the presence of self-interaction error and absence of long range electron-electron interactions. However, a number of self-interaction-free DFT functionals exists in the literature, which also includes long range electron-electron interactions such as CAM-B3LYP, wB97XD and M06HF. Therefore, realizing the need of the present work, we have used four different DFT functionals: B3LYP, CAM-B3LYP, M06HF, and wB97XD, to explore electron dynamics following ionization of halogen bonded clusters: ACI:NH$_3$. It is also found by us and others that often inclusion of many-body effects is important for more meaningful investigation of electron dynamics following ionization and, therefore, one has to go beyond the single-determinant approximation for the ionic states. The complete active space self-consistent field (CASSCF) theory uses a restricted active space for building the determinantial expansions of the electronic states and thus satisfactorily introduces static electron-electron correlation in the description of charge migration. Furthermore, additional dynamical electron-electron correlation can be incorporated by using complete active space perturbation (e.g., CASPT2 or CASMP2) theory. Therefore, in this work, we have also employed the CASSCF-based methodologies, along with the DFT methodology, for meaningful comparison.

The exploration of the neutral and cationic (ground and ion states, respectively) Potential Energy Surfaces (PESs) of ACI:NH$_3$ complexes is performed at both the DFT and at the CASSCF levels of theory. For CASSCF calculations different active spaces are used for different ACI:NH$_3$ complexes, which are shown in Figure S1-S6 in supplementary material. All geometry optimizations and ionization energy calculations are executed using the Gaussian 09 package. The stability of each critical-point structure is tested by calculating the analytical frequencies except for the conical intersection point. The conical intersection optimization calculation, performed at the CASSCF level and implemented in Gaussian09, is state-averaged by default. The lowest energy point on the conical intersection seam, called lowest energy conical intersection, is optimized and localized using a projected gradient algorithm, as implemented in Gaussian 09. In this search, the energy of the excited state is minimized. At the same time, the energy difference between the excited state and the closest lower energy state is minimized. Transition state is identified by one representative imaginary frequency corresponding to an unstable normal mode of vibration.

The binding energy of the halogen bonded complex is calculated as the difference between the sum of the monomer energies and complex energy. For the correction of interaction...
energy from the inherent basis set superposition error (BSSE), a counterpoise method\textsuperscript{26} is used for all complexes. The theory of “atoms in molecules (AIM)"\textsuperscript{27} has been used to analyze the topology of all the optimized complexes with the help of AIMAll\textsuperscript{28} program. The presence of a bond critical point (BCP) and the bond path between X and B atoms in the X non-covalent bond is considered to be one of the important criteria in support of existence of X-noncovalent bonding interactions.\textsuperscript{29} To investigate charge migration phenomena at larger halogen bond distance, we have examined this electron density topology-based criterion along with halogen bonding interaction energy for the respective halogen bonded complex.

A. Charge migration dynamics at the vertical ion (VI) point

Vertical ionization of a neutral halogen bonded complex produces a non-stationary electronic state which evolves in time. At the VI point, the geometry of the complex, however, remains unchanged. Vertical ionization creates a localized hole in the complex. If the electron is removed from highest occupied molecular orbital (HOMO), then the initial hole is created at the HOMO. However, as HOMO of the neutral complex is not a stationary orbital of the cation, the hole charge density evolves in time. The time propagation of the hole density can be monitored by projecting the HOMO of the neutral on the stationary molecular orbitals of the cation at the fixed VI geometry of the complex. This procedure of probing charge migration dynamics was first introduced by Levine and Remacle\textsuperscript{172} and we have closely followed their procedure, as presented below. Any molecular orbital (|Ψ\textsubscript{λ}\rangle) can be expressed as a linear combination of the atomic basis orbitals (called LCAO method), i.e.,

|Ψ\textsubscript{λ}\rangle = \sum_{i=1}^{N} C_{i\lambda} |\Theta_{i\lambda}\rangle. \quad (1)

Here, |\Theta_{i\lambda}\rangle is the \(i\)th atomic orbital of the \(\lambda\)th molecular orbital and \(C_{i\lambda}\) is the respective expansion coefficient. The cationic molecular orbitals are computed under the unrestricted-self consistent field (unrestricted-SCF) scheme, which yields separate molecular orbitals for \(\alpha\) and \(\beta\) spins. After removal of an electron from the HOMO of the neutral (featuring the vertical ionization of the neutral halogen bonded complex), a localized hole is created. To time-propagate the hole density, the HOMO of the neutral can be projected onto all the stationary cationic molecular orbitals and then a time dependent phase factor \(e^{-iE_{\text{HOMO}}t} \) can be introduced to the final equation of the hole orbital. Under the unrestricted scheme, the HOMO orbital of the neutral is projected both onto the \(\alpha\)-cationic orbitals and onto the \(\beta\)-cationic orbitals, separately. At time \(t = 0\), therefore, the hole orbital can be represented as

|Ψ\textsubscript{α}(0)\rangle = \sum_{k=1}^{N} \langle \Phi_{\alpha k} | Ψ\textsubscript{HOMO} | \Phi_{\alpha k}\rangle, \quad (2a)

|Ψ\textsubscript{β}(0)\rangle = \sum_{k=1}^{N} \langle \Phi_{\beta k} | Ψ\textsubscript{HOMO} | \Phi_{\beta k}\rangle. \quad (2b)

Here, \(Ψ\textsubscript{HOMO}\) is the canonical HOMO of the neutral, \(Φ\textsubscript{λ}\) is the \(\lambda\)th cationic molecular orbital, and \(|Ψ\textsubscript{α}(0)\rangle\) and \(|Ψ\textsubscript{β}(0)\rangle\) are the hole orbitals with spin labels \(\alpha\) and \(\beta\), respectively. Both \(Ψ\textsubscript{HOMO}\) and \(Φ\textsubscript{λ}\) can be expanded as the linear combination of atomic basis orbitals which is given by Eq. (1) (under LCAO scheme). At a later time \(t\), the hole orbitals associated with two spins can be represented (by introducing the time dependent phase factor) as

|Ψ\textsubscript{α}(t)\rangle = \sum_{k=1}^{N} \langle \Phi_{\alpha k} | Ψ\textsubscript{HOMO} | e^{-iE_{\text{HOMO}}t} | \Phi_{\alpha k}\rangle, \quad (3a)

|Ψ\textsubscript{β}(t)\rangle = \sum_{k=1}^{N} \langle \Phi_{\beta k} | Ψ\textsubscript{HOMO} | e^{-iE_{\text{HOMO}}t} | \Phi_{\beta k}\rangle. \quad (3b)

Substituting Eqs. (3a) and (3b) by Eq. (1), for \(Ψ\textsubscript{HOMO}\) and \(Φ\textsubscript{λ}\), we get

|Ψ\textsubscript{α}(t)\rangle = \sum_{k=1}^{N} \sum_{i=1}^{N} C_{i\alpha} C_{i\lambda} | e^{-iE_{\text{HOMO}}t} | C_{i\lambda} | Ψ_{i\lambda}\rangle, \quad (4a)

|Ψ\textsubscript{β}(t)\rangle = \sum_{k=1}^{N} \sum_{i=1}^{N} C_{i\beta} C_{i\lambda} | e^{-iE_{\text{HOMO}}t} | C_{i\lambda} | Ψ_{i\lambda}\rangle. \quad (4b)

The sum in Eqs. (4a) and (4b) is over all \(N\) stationary cationic orbitals which include both occupied and unoccupied orbitals. The time propagation of the hole orbital following Eqs. (4a) and (4b) is performed at the DFT level of theory.

In order to perform dynamics calculations, therefore, the following steps are followed. The expansion coefficients of the HOMO and the cationic orbitals are, first, taken from the single point SCF-calculated population analysis of the neutral and the cation of ACI:NH\textsubscript{3} complex, respectively, at the vertical point. Then, we carry out the symmetry orthogonalization of the atomic orbitals. Thereafter, the HOMO of the neutral is projected onto the cationic orbitals according to Eqs. (2a) and (2b) by matrix multiplication performed with FORTRAN program. The time-dependent exponential factor is then imposed on both equations by multiplying these equations with respective cosine and sine functions. Finally, to visualize the hole density at a certain time following ionization, the squared cosine and sine functions are added using the cubman program implemented in Gaussian09.\textsuperscript{25}

III. RESULTS AND DISCUSSION

A. Structures and binding energies of halogen bonded ACI⋯NH\textsubscript{3} complexes

Recent works on halogen bonding show that second order Möller-Plesset (MP2) perturbation theory and density functional theory with B3LYP functional can predict the neutral ground state geometries of halogen bonded clusters with reasonable accuracy.\textsuperscript{13} They have also been known to accurately describe halogen bonding interactions in Cl-containing clusters.\textsuperscript{30} Therefore, the geometrical structures of different halogen bonded systems, containing CI atom, optimized on the neutral potential energy surface, are calculated at the MP2 and B3LYP levels of theory with the reasonably large 6-31+G(d,p)
basis set. Optimized geometries are depicted in Figure 1, along with some relevant structural parameters.

All the neutral clusters exhibit halogen bonding interactions: all the Cl⋯N halogen bond distances are predicted to be in the range of ca. 2–3 Å. As often an important characteristic of any noncovalent interaction is considered to be the strength of the interaction, Figure 2 illustrates binding energies of ACl⋯NH₃ complexes as a function of Cl⋯N halogen bond distance, computed at the MP2/6-31+G(d,p) and B3LYP/6-31+G(d,p) levels of theory with BSSE corrections. To place this plot for halogen bonds in the context of the well-conceived hydrogen bond, the hydrogen bond energy (ca. 4 kcal/mol) of the water dimer in the gas phase is also plotted in the same graph. It is evident in the figure that the FCl:NH₃ complex exhibits the highest binding energy and the H₂NCl:NH₃ complex features the lowest binding energy. It is also worth noting that with more electron withdrawing substituent (or more electronegative substituent, A), there is a steady increase in halogen bond energy. More discussion on the binding energy versus halogen bond length can be found in many recent literatures and we shall revisit the same later in this paper.

**B. NCCI:NH₃**

The removal of an electron via vertical photoionization of neutral NCCI⋯NH₃ complex creates doublet radical cation. Table 1 gives the energies associated with the vertical ionization (at the VI-points of the respective surfaces) of NCCI⋯NH₃ complex to the D₀ and D₁ cationic states from the neutral singlet state (S₀), which are calculated at the respective level of theory. The vertical ionization energy to the D₀ state is estimated by subtracting their respective electronic energies from that of the optimized neutral S₀ state geometry. Here, zero-point energy correction to the vertical ionization energy is not done because the vertical radical cation state (VI) is not a stable point on the cationic PES; thus, zero point energy at VI point is meaningless.

At all the DFT levels of theory, the vertical ionization energies to D₀ ion states of NCCI⋯NH₃ complex are estimated to be in the range of ca. 10.5-12 eV. Compared to B3LYP, CAM-B3LYP, and wB97xD functionals, the M06HF long range corrected-functional (which contains 100% HF exchange correlation at all ranges) yields vertical ionization energy which is very close to that obtained at higher levels, such as MP2, CASSCF, and CASMP2.

At the DFT method, the cationic states are represented by KS orbitals resulting from solving the cationic KS-DFT equations. The DFT-self-consistent field (DFT-SCF) calculation results in hierarchical ordering of the orbitals in terms of KS orbital energies, and upon performing SCF-iteration, it is possible to identify the canonical orbital associated with different eigen values. Under restricted DFT-SCF scheme, for singlet neutral system, highest energy canonical molecular orbital possesses two electrons, which is often called HOMO. Ionization of singlet neutral system results in the respective doublet cationic state and arguably, it is better to use unrestricted scheme to describe the cationic state at the DFT level because under unrestricted SCF-scheme, electrons of different spins are allotted to stay at different orbitals and thus, it enables electrons of opposite spin to keep away from one another, incorporating the average role of the Coulomb repulsion. When the cation is computed under the unrestricted SCF-scheme, its orbitals also carry a spin level, say α or β. Following ionization, the hole orbital is
TABLE I. Relative energies (with respect to neutral ground state optimized geometry) of the critical points at the cationic potential energy surfaces of NCCl:NH$_3$ complex, computed at different levels of theory. CASMP2 energies are obtained at the CASSCF-optimized geometries. Energies are given in eV (within bracket the energies are given in kcal/mol).

<table>
<thead>
<tr>
<th>Critical point</th>
<th>B3LYP</th>
<th>M06HF</th>
<th>CAM-B3LYP</th>
<th>wB97XD</th>
<th>MP2</th>
<th>CASSCF(8,6)</th>
<th>CASMP2(8,6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VI $D_0$</td>
<td>10.75</td>
<td>12.12</td>
<td>11.15</td>
<td>11.12</td>
<td>12.03</td>
<td>11.56</td>
<td>12.35</td>
</tr>
<tr>
<td></td>
<td>(247.90)</td>
<td>(279.49)</td>
<td>(257.12)</td>
<td>(256.43)</td>
<td>(277.41)</td>
<td>(266.58)</td>
<td>(284.79)</td>
</tr>
<tr>
<td>VI $D_1$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(D$_1$/D$<em>0$)$</em>{CI}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AI-1</td>
<td>10.05</td>
<td></td>
<td>10.21</td>
<td>10.15</td>
<td></td>
<td>11.36</td>
<td>11.72</td>
</tr>
<tr>
<td></td>
<td>(231.75)</td>
<td></td>
<td>(235.44)</td>
<td>(234.06)</td>
<td></td>
<td>(261.96)</td>
<td>(270.27)</td>
</tr>
<tr>
<td>AI-2</td>
<td>10.15</td>
<td></td>
<td>10.23</td>
<td>10.17</td>
<td></td>
<td>9.16</td>
<td>9.89</td>
</tr>
<tr>
<td></td>
<td>(234.06)</td>
<td></td>
<td>(235.90)</td>
<td>(234.52)</td>
<td></td>
<td>(211.23)</td>
<td>(207.31)</td>
</tr>
<tr>
<td>TS</td>
<td>9.16</td>
<td>9.37</td>
<td>9.15</td>
<td>9.16</td>
<td></td>
<td>8.73</td>
<td>7.86</td>
</tr>
<tr>
<td></td>
<td>(211.23)</td>
<td>(216.08)</td>
<td>(211)</td>
<td>(211.23)</td>
<td></td>
<td>(201.32)</td>
<td>(201.32)</td>
</tr>
</tbody>
</table>

represented by the canonical lowest unoccupied $\beta$ molecular orbital (LUMO $\beta$).

The canonical HOMO of neutral NCCl$\cdots$NH$_3$ and the canonical LUMO $\beta$ at the VI point on the $D_0$ surface, as computed at different DFT levels of theory, are depicted in Figure 3. At all the levels of theory, the HOMO of the neutral NCCl$\cdots$NH$_3$ complex clearly exhibits charge (electron) density mostly distributed on the NH$_3$-end of the complex. Therefore, immediately following vertical ionization, the hole resides on the NH$_3$-end of the complex. The LUMO $\beta$ at the

(a) Theory | HOMO (neutral) | LUMO $\beta$ (cation) | SONO (cation)
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP</td>
<td>![B3LYP Image]</td>
<td>![B3LYP Image]</td>
<td>![B3LYP Image]</td>
</tr>
<tr>
<td>CAM-B3LYP</td>
<td>![CAM-B3LYP Image]</td>
<td>![CAM-B3LYP Image]</td>
<td>![CAM-B3LYP Image]</td>
</tr>
<tr>
<td>M06HF</td>
<td>![M06HF Image]</td>
<td>![M06HF Image]</td>
<td>![M06HF Image]</td>
</tr>
<tr>
<td>wB97XD</td>
<td>![wB97XD Image]</td>
<td>![wB97XD Image]</td>
<td>![wB97XD Image]</td>
</tr>
</tbody>
</table>

(b) Theory | HOMO (neutral)/HONO | SOMO/SONO (cation)
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CASSCF(8,6) (Canonical orbital)</td>
<td>![CASSCF(8,6) CAN Image]</td>
<td>![CASSCF(8,6) CAN Image]</td>
</tr>
<tr>
<td>CASSCF(14.9) (Natural Orbital)</td>
<td>![CASSCF(14.9) NAT Image]</td>
<td>![CASSCF(14.9) NAT Image]</td>
</tr>
</tbody>
</table>
VI points on the D₀ surface, on the other hand, illustrates that the hole density is localized on the CICN-end of the complex. More specifically, DFT results with functionals, such as wB97XD, CAM-B3LYP, and B3LYP, show that the hole density is delocalized over both the NH₂- and CICN-ends of the complex. On the other hand, the DFT result with M06HF functional exhibits that the hole density is localized purely on the CICN-end of the complex. This is probably due to the fact that the M06HF functional possesses the highest (100%) HF exchange correlation at all ranges, pointing to the importance of exchange correlation in the hole migration phenomenon. Furthermore, this also proves the fact that the M06HF functional significantly localizes the KS-orbitals, which is very similar to the orbitals computed at electron correlation methods (e.g., CASSCF).

In the present work, the SCF-variational orbital optimization method is used to identify the canonical HOMO of neutral NCCI · · · NH₃ complex and the LUMO β of cationic NCCI · · · NH₃ complex. Similar methodology was, first, used by Levine, Remacle, and co-workers in the context of ultrafast hole migration in molecules following vertical ionization and later by us along with Infrared-vacuum ultraviolet (IR-UV) photoionization spectroscopy. Our previous work and Levine’s previous work show that the SCF-orbital optimization methodology can efficiently predict the hole migration in isolated peptides and amino acids following their vertical ionization. In this context, we note that another methodology of treating multiple configurations in cation is presented in the literature using Greens function-based methods, as demonstrated by Cederbaum and his co-workers.

In the above discussion, we have stated that if the cation is computed under the unrestricted-SCF scheme, the hole resides in the canonical LUMO β, following ionization of the neutral complex. For unambiguous assignment of the hole orbital in radical cation, however, we have also analysed natural orbitals, which are eigenvectors of density operator. Natural orbitals exhibit occupancy number and when natural orbitals are computed for doublet cationic state, the highest occupied molecular orbital houses one single electron, which is called singly occupied (occupancy number 1) natural orbital (SONO). Figure 3 illustrates that the LUMO βs and the SONOs of the cationic NCCI · · · NH₃ complex are nearly identical at different levels of theory.

As the DFT is essentially a monoconfigurational method, it is blind to the electronically excited cationic states which may be present in close proximity to the electronically ground cationic state surface. In this regard, multi-configurational methodology, e.g., the CASSCF theory (which can explore non-adiabatically coupled electronic state surfaces), is more appropriate for a more rigorous description of the potential energy surfaces, particularly when the upper excited electronic cationic state surfaces are present in close proximity to the ground cationic state surface. This is why we have also calculated the vertical ionization energy of NCCI · · · NH₃ complex at the CASSCF level of theory with diffuse basis set 6-31+G(d,p) and have found that the vertical ionization energy to the D₀ and D₁ states is associated with 11.56 and 11.81 eV, respectively. Furthermore, in order to include dynamic electron-electron correlation in the CASSCF calculation (CASSCF only includes static correlation), we have calculated the ionization energy of NCCI · · · NH₃ complex at the CASMP2/6-31+G(d,p) level of theory, which predicts the ionization energies of 12.35 eV and 12.51 eV for the D₀ and the D₁ states, respectively. Comparing these results, obtained at the CASSCF/6-31+G(d,p) and the CASMP2/6-31+G(d,p), one can unambiguously state that the D₀ and D₁ cationic states are very closely lying (within 0.2-0.3 eV).

Identification of canonical HOMO of neutral complex is quite straight-forward at the DFT level of theory (as shown in the preceding discussion) as it is associated with highest orbital energy. However, at the CASSCF level of theory, definition of HOMO is misleading because the CASSCF canonical orbitals cannot be associated with unique eigen values, and as a result, hierarchical ordering of orbitals in terms of orbital energies is not possible at the CASSCF level. Hence, identification of the canonical HOMO among all the CASSCF canonical orbitals becomes ambiguous. In order to assign canonical HOMO at the CASSCF level of theory, however, we have first identified the canonical HOMO at the DFT level and then among all the CASSCF canonical molecular orbitals, the one resembling the DFT-computed HOMO was chosen as the CASSCF HOMO as depicted in Figure 3. This gives us confidence in predicting canonical HOMO at the CASSCF level unambiguously. This simple scheme is further corroborated by the fact that the CAS-wave function for the neutral NCCI · · · NH₃ complex is mostly of a single reference character (which is concluded upon inspection of the coefficients for the configuration state functions on the ground state surface).

Identification of canonical singly occupied molecular orbitals (SOMO) and SONO at the CASSCF level, however, is quite straight-forward. To identify canonical SOMO at the VI point on the D₀ and D₁ surfaces at the CASSCF level, we have chosen that canonical orbital of cationic NCCI · · · NH₃ complex as SOMO, for which the diagonal term shows a value of 1 (which is indicative of occupation number 1) in the one electron density matrix generated by the CAS calculation. The CASSCF canonical HOMO of neutral NCCI · · · NH₃ complex and canonical SOMO of cationic NCCI · · · NH₃ complex at the VI point on both D₀ and D₁ cationic surfaces exhibit, as illustrated in Figure 3, in concordance with the DFT results, that the hole migrates from the NH₂-end to the CICN-end of the complex. The SONO at the CASSCF level, which is also identified by occupancy number 1, features similar electron density to that of canonical SOMO, which is illustrated in Figure 3. In cases where the one electron density matrix generated by the CASSCF calculation is diagonal, the canonical orbitals and natural orbitals become equivalent and also the diagonal terms correspond to the approximate occupation number of the corresponding orbital. This was indeed the case for the VI point on both the D₀ and D₁ cationic surfaces of NCCI · · · NH₃ complex, where all the off-diagonal terms of the density matrix nearly vanish (i.e., values are on the order of 10⁻⁴-10⁻⁸). Therefore, the diagonal term (approximate occupation number) having the value closest to 1 corresponds to a canonical orbital which is singly occupied (SOMO). In our study, the diagonal term corresponding to the SOMO shows a value equal to 1 (correct up to at least 3 decimal places) for all the critical points on the doublet cationic PESs and therefore, both the SONO

Reference: 31
and canonical SOMO at the VI point are found to be nearly identical, in concordance with the fact that the one electron density matrix is nearly diagonal at the VI point on the radical cationic PESs. Therefore, we believe that our prediction of singly occupied molecular orbital (either SOMO or SONO) at the CASSCF level is unambiguous.

Thus, detailed analysis of both the canonical and the natural orbitals of NCCI···NH₃ complex at different levels of theory (DFT and CASSCF) suggests that upon vertical ionization of NCCI···NH₃ complex, the hole migrates from the NH₃-end to the CICN-end of the halogen bonded NCCI···NH₃ complex at the VI point (frozen nuclear configuration) on the D₀ surface. The same is predicted at the VI point on the D₁ cationic surface as well, at the CASSCF level of theory. This hole migration is not coupled with the nuclear motion; instead, it is brought about solely by electron-electron correlation and relaxation effects through the halogen bond. Dynamics of this purely electron correlation driven-hole dynamics is discussed below.

Immediately following vertical ionization (to the VI point on the D₀ surface), the canonical HOMO of the neutral NCCI···NH₃ complex represents the hole orbital (which gives hole density). The subsequent time-propagated hole orbital at the VI-geometry is determined by appending the time-dependent phase to each orbital of the cation in Eq. (2) of the hole orbital. The sum in this equation is overall 95 orbitals of the cation, which includes both occupied and unoccupied cationic orbitals. Figure 4 shows the hole dynamics in halogen bonded NCCI···NH₃ complex. The hole dynamics is computed using unrestricted-wB97XD/6-31+G(d,p) orbitals of the NCCI···NH₃ cation at the VI point on the D₀ surface. For ionization from the HOMO, that is purely localized on the NH₃-end and has a clear non-bonding character, the hole moves rapidly and reaches the CICN-end through the halogen bond in approximately 0.5 fs. This computed time scale of hole migration due to removal of an electron from HOMO is in qualitative agreement with the hole migration time scale in small molecules determined by Cederbaum and co-workers, and Levine, Remacle, and co-workers. Another long-range corrected DFT functional, CAM-B3LYP, renders similar time scale for the charge migration dynamics through the halogen bond in NCCI:NH₃ complex, as shown in Figure S7 in supplementary material.

Experiments demonstrating electron dynamics with direct application of attosecond pulses in a halogen bonded molecular system have not been performed yet; however, several indirect experimental demonstrations of attosecond electron migration or delocalization over another non-covalently bonded system, namely, hydrogen bonded network, are documented already in the literature. For instance, an increasingly popular X-ray absorption technique named “core-hole clock” spectroscopy has already pointed out a very interesting and profound mechanism of electron delocalization (and migration) in liquid water and ice which exhibits hydrogen bonds (one of the most conceived noncovalent bonds). This work shows that an excess electron propagates through organized hydrogen-bonded network within 0.5 fs (or 500 as). Quite interestingly, this time scale, which is observed for hydrogen bonds, is also comparable to what we have predicted for halogen bonds.

We anticipate and strongly hope that in the near future, with the help of emerging attosecond pulses, charge migration dynamics through halogen bonds (as well as other unconventional noncovalent bonds, such as chalcogen, pnicogen, and tetrel bonds) would also be estimated and our present theoretical work on halogen bonds would serve as a starting point of thinking for that novel experimental demonstration.

After identifying the hole density at the vertical ion points, we have explored subsequent reactivity of the NCCI···NH₃ complex on the cationic potential energy surfaces to find out the possible role of specific localization of the hole in the subsequent reactivity of the nascent NCCI···NH₃ radical cation. The energy profile diagrams of NCCI···NH₃ complex on the cationic potential energy surfaces, computed at the wB97XD/6-31+G(d,p) and at the CASSCF/6-31+G(d,p), are illustrated in Figures 5 and 6, respectively. The VI point on the doublet cationic surface is not a stationary state and, therefore, the nascent radical cation of NCCI···NH₃ complex starts evolving on the D₀ or D₁ surface, following vertical ionization to the respective ion states.

Both the DFT and CASSCF levels of theory, as evident in Figures 5 and 6, suggest that the halogen bonding interaction is no longer stable on the cationic potential energy surface of NCCI···NH₃. On the D₀ cationic surface, strength of hydrogen bonding interaction (configuration AI-2, featuring
CICN⋯H2N hydrogen bond) dominates over that of the halogen bonding interaction (configuration VI, featuring NCCI⋯NH3 halogen bond). On the cationic D0 surface, the hydrogen bonded CICN⋯H2N configuration is stabilized by more than 45 kcal/mol with respect to the halogen bonded NCCI⋯NH3 configuration. However, on the neutral ground state potential energy surface of the complex, halogen bonded NCCI⋯NH3 configuration is the most stable conformer and it is stabilized by more than ~2.7 kcal/mol with respect to the hydrogen bonded CICN⋯H2N configuration. The relative energies of all the critical points on the D1 and D0 surfaces with respect to the neutral ground state optimized geometry energy are summarized in Table I.

Recent literature\(^{11}\) shows that the ground cationic surface topography can often be affected by the proximity of the upper electronically excited cationic state surfaces near the conical intersection region. Therefore, in the present work, we have utilized CASSCF theory to explore conical intersection between the D1 and the D0 states, which explores the relaxation pathway of the cationic NCCI⋯NH3 complex from the VI point on the D1 surface to the D0 surface.

The canonical SOMOs, computed at the (D1/D0)\(\text{C1}\) conical intersection point for both the D0 and D1 surfaces, as depicted in Figure 6, show that hole density stays localized at the CICN-end of the complex, similar to the VI point. As the molecular orbital signs on CICN-moiety at the (D1/D0)\(\text{C1}\) and the VI point of the D1 state are the same, it can be concluded that the (D1/D0)\(\text{C1}\) state originates from the D1 VI point. Furthermore, slight reorganization of the NCCI⋯NH3 complex structure is also observed at the (D1/D0)\(\text{C1}\) point with respect to the VI point structure, as depicted in Figure 6. The halogen bond distance at the (D1/D0)\(\text{C1}\) is computed to be 2.69 Å, whereas, the same at the VI point exhibits 3.11 Å. The <CCI⋯N bond angle is calculated to be 177° at the (D1/D0)\(\text{C1}\) point, whereas the same features 180° at the respective VI point. The (D1/D0)\(\text{C1}\) geometry (see Figure 6) exhibits reduction in the NCCI⋯NH3 halogen bond distance. This could be due to the fact that the hole localization at the CICN moiety makes it a stronger electron acceptor (we note that NH3 is the lone pair donor in the halogen bonded complex) and, in turn, this stabilizes the halogen bond between the NH3 and the CICN moieties. It is also important to notice that the hole is eventually transferred back to the NH3 moiety (see Figure 6) which makes NH3 a strong acid, favouring strong hydrogen bond between the NH3 and CICN moieties. After a non-adiabatic surface crossing through (D1/D0)\(\text{C1}\), the NCCI⋯NH3 radical cation relaxes to the hydrogen bonded CICN⋯H2N adiabatic ion structure (AI-2) on the D0 surface, which is predicted at the CASSCF level of theory. The optimized structure and SOMO density at AI-2 show a significant change in both geometry and hole density as compared to that of the (D1/D0)\(\text{C1}\), which is clearly indicated in Figure 6. The CASMP2 level of theory also predicts similar results, as indicated in Table I.

The pathway associated with the conversion of the halogen bonded configuration NCCI⋯NH3 to the hydrogen bonded configuration CICN⋯H2N on the D0 cationic surface is predicted to be a downhill process both at the CASSCF and DFT levels of theory (wB97X-D results are illustrated in Figure 5). However, DFT predicts a few additional critical points which ultimately lead the halogen bonded configuration NCCI⋯NH3 to the hydrogen bonded configuration CICN⋯H2N. The adiabatic ion AI-1 geometry and transition state TS geometries are localized at the DFT level of theory. The wB97XD-results, as depicted in Figure 5, exhibit an activation energy barrier of only 0.46 kcal/mol with respect to the AI-1 point. This small activation barrier features a transition state for conversion of halogen bonded configuration to hydrogen bonded configuration. The LUMO \(\beta\) densities (see Figure 5) at the optimized geometry of AI-1 and TS are found to be localized at both NH3 and CICN-ends of the complex. However, the LUMO \(\beta\) density at the optimized geometry of AI-2 (the hydrogen bonded conformer) exhibits the hole density localized on the NH3-end of the complex. This DFT result is in agreement with the CASSCF-results.
Thus, the reaction pathways stated above along with the hole density plots at different critical points on the cationic PESs of NCCI \( \cdots \) NH\(_3\) complex, which are summarized in Figures 5 and 6 for two different levels of theory, wB97XD (DFT) and CASSCF, respectively, corroborate the fact that the reactivity of halogen bonded NCCI \( \cdots \) NH\(_3\) complex, following vertical ionization (removal of outermost electron), can be hole-directed and a hole migration at the VI point may have preluding effect in defining chemical reaction dynamics of NCCI \( \cdots \) NH\(_3\) on its doublet cationic potential energy surfaces. From a broader perspective, both the DFT and CASSCF methodologies suggest that the orbital localized on the NH\(_3\)-end (in-plane orbital) is polarized to out-of-plane orbital, (see Figure 4) within 500 as time scale upon vertical ionization. This polarization of change might be the driving force for conformer switching on the cationic potential energy surface. A nuclear motion coupled electron dynamics calculation is now required to obtain more details of predicted charge-directed reactivity of halogen bonded complex NCCI \( \cdots \) NH\(_3\).

In the present context, another seemingly interesting question remains unaddressed. On the ground neutral surface, NCCI: NH\(_3\) complex exhibits not only Cl \( \cdots \) N halogen bonding interaction but also N \( \cdots \) H hydrogen bonding interaction. The hydrogen bonded configuration of NCCI: NH\(_3\) complex is not the most stable conformer; however, it is interesting to examine the cationic surfaces created by hydrogen bonded conformer following vertical ionization. For the sake of brevity of the present article, however, this is discussed in Figure S8 in supplementary material.\(^{24}\)

### C. ACI: NH\(_3\) (A = F, OH, CF\(_3\), NH\(_2\), and COOH)

In this article, we have already presented that the strength of halogen bonding interaction in ACI: NH\(_3\) complexes (where A features F, OH, CN, CF\(_3\), NH\(_2\), and COOH) varies significantly with the substituents. Among the halogen bonded complexes studied here, FCI: NH\(_3\) complex exhibits the strongest Cl \( \cdots \) N halogen bonding interaction and H\(_2\)NCI: NH\(_3\) features the weakest Cl \( \cdots \) N halogen bonding interaction. Undoubtedly, finding the reason behind this substituent-dependent strength of halogen bonds can be the subject of a self-contained investigation, which is discussed in the recent literature to some extent;\(^{13}\) however, our motivation in the present work is to examine the effect of the halogen bonding strength on the electron-electron correlation- and relaxation-driven charge (hole) migration dynamics in halogen bonded complexes. To achieve this goal, we have compared and contrasted the hole density distributions at the VI point on the D\(_0\) cationic PESs of different ACI \( \cdots \) NH\(_3\) complexes. As wB97XD\(^{23}\) is a self-interaction-free DFT functional which also includes long range electron-electron interactions (recent study\(^{22b}\) by Levine and co-workers shows that both factors can play an important role in describing the hole migration dynamics in molecules following ionization), for this comparative study we have selected wB97XD/6-31+G(d,p) level of theory. In addition, as the CASSCF theory includes electron-electron correlation by building the determinantal expansions of the electronic states, CASSCF/6-31+G(d,p) level of theory is also employed to make this comparative study more rigorous (and reliable).

<table>
<thead>
<tr>
<th>Complexes</th>
<th>wB97XD/6-31+G(d,p)</th>
<th>CASSCF/6-31+G(d,p)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HOMO (neutral)</td>
<td>LUMO ( \beta) (cation)</td>
</tr>
<tr>
<td>FCl: NH(_3)</td>
<td><img src="image1" alt="Image" /></td>
<td><img src="image2" alt="Image" /></td>
</tr>
<tr>
<td>HOCl: NH(_3)</td>
<td><img src="image7" alt="Image" /></td>
<td><img src="image8" alt="Image" /></td>
</tr>
<tr>
<td>NCCI: NH(_3)</td>
<td><img src="image13" alt="Image" /></td>
<td><img src="image14" alt="Image" /></td>
</tr>
<tr>
<td>H(_2)NCCI: NH(_3)</td>
<td><img src="image19" alt="Image" /></td>
<td><img src="image20" alt="Image" /></td>
</tr>
<tr>
<td>F(_2)CCI: NH(_3)</td>
<td><img src="image25" alt="Image" /></td>
<td><img src="image26" alt="Image" /></td>
</tr>
<tr>
<td>HOOCCl: NH(_3)</td>
<td><img src="image31" alt="Image" /></td>
<td><img src="image32" alt="Image" /></td>
</tr>
</tbody>
</table>

**FIG. 7.** Neutral HOMO, cationic LUMO \( \beta\), and SONO (calculated at the wB97XD/6-31+G(d,p) level of theory) for different ACI: NH\(_3\) complexes are illustrated. The CASSCF/6-31+G(d,p)-computed canonical HOMO and SOMO are also shown for the same complex.
Figure 7 depicts the canonical HOMO of the neutral, and the canonical LUMO β and the SONO of the cationic ACl:NH₃ complexes, as computed at the wB97XD/6-31+G(d,p) level of theory. It is quite clear in the figure that the SONO density and the LUMO β density are the same for a particular complex. Furthermore, the neutral HOMO and the cationic LUMO β densities remain the same for only FCl:NH₃ and HOCl:NH₃ complexes, which is suggestive of no charge migration following ionization of these complexes to the D⁰ cation state. However, all other complexes, including NCCI:NH₃, H₂NCCI:NH₃, F₃CCl:NH₃, and HOOCOCI:NH₃, exhibit different HOMO and LUMO β densities, which is an indication of charge migration following ionization to the respective D⁰ state. In particular, analysis of the neutral HOMO density and cationic LUMO β density of these complexes suggests that the charge (hole) migrates from the NH₃-end of the complex to the ACl-end of the complex for NCCI:NH₃, F₃CCl:NH₃, and HOOCOCI:NH₃ complexes. On the contrary, H₂NCCI:NH₃ complex features a charge migration from H₂NCI-end of the complex to the NH₃-end of the complex. Figure 8 illustrates the hole migration dynamics following vertical ionization (from neutral HOMO) of H₂NCI:NH₃, F₃CCl:NH₃, and HOOCOCI:NH₃ halogen bonded complexes, computed at the unrestricted wB97XD/6-31 +G(d,p) level of theory. This figure clearly corroborates the fact that, following removal of an electron from the neutral HOMO of these complexes (vertical ionization), hole migrates from one end to the other end of the complex through the halogen bond in approximately 0.5-0.6 fs. The time evolution of the hole densities in these complexes is also computed at the CAM-B3LYP/6-31+G(d,p) level of theory, which is shown in Figure S7 in supplementary material.²⁴

Therefore, the above results suggest that the natural time scale for hole migration through halogen bonds can be on the order of 0.5-0.6 fs. However, two questions remain unanswered in this context: why do not NH₃-complexes with CIF and CIOH show charge migration at the VI point and why are the HOMO densities different for different NH₃-containing complexes? The HOMO density is distributed purely (or sometimes dominantly) on the ACl moiety for complexes with CIF, CIOH, and CINH₂ molecules; whereas, the HOMO density is localized purely (or mostly) on the NH₃ moiety for complexes with CICN, CICF₃, and CICOOH molecules.

In order to address the above two questions, first, we examine the ionization energies of all isolated complex-forming-constituents, which are given in Table II. The ionization energy of isolated H₂NCl molecule is lower than that of isolated NH₃ molecule and, therefore, it is expected that the HOMO density should be localized on the H₂NCl-end of the H₂NCl:NH₃ complex, which is also evident in Figure 7. On the other hand, we find that isolated NH₃ molecule exhibits the lowest ionization energy among other isolated molecules CIF, CIOH, CICN, CICF₃, and CICOOH. Therefore, it can be expected that FCl:NH₃, HOCl:NH₃, NCCI:NH₃, F₃CCI:NH₃, and HOOCOCI:NH₃ complexes should feature the HOMO localized on the NH₃-end of the respective complex. Indeed, the neutral HOMO densities are localized (mostly) on the NH₃-end of the NCCI:NH₃, F₃CCI:NH₃, and HOOCOCI:NH₃ complexes, as evident in Figure 7. Quite counter-intuitively, however, Figure 7 depicts that the neutral HOMO density is localized on the FCI- and HOCl-ends of the FCl:NH₃ and HOCl:NH₃ complexes, respectively. To give a rational explanation (computational proof is given in the next paragraph), we say that due

FIG. 8. Snapshots of the time-evolution of the hole density following removal of an electron from HOMO of neutral ACl:NH₃ complexes for initial 1-1.2 fs, computed at wB97XD/6-31+G(d,p).
TABLE II. Vertical ionization energies (eV) of isolated NH$_3$, CIF, ClOH, ClCN, ClNH$_2$, ClCF$_3$, and ClCOOH molecules, computed at the MP2/6-31+G(d,p) level of theory. Experimental results are also given, if available.

<table>
<thead>
<tr>
<th>Molecules</th>
<th>IE (theoretical)</th>
<th>IE (experimental)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_3$</td>
<td>10.55</td>
<td>10.10</td>
</tr>
<tr>
<td>F$-$Cl</td>
<td>12.87</td>
<td>12.77</td>
</tr>
<tr>
<td>HO$-$Cl</td>
<td>10.93</td>
<td>11.12</td>
</tr>
<tr>
<td>NC$-$Cl</td>
<td>12.68</td>
<td>12.37</td>
</tr>
<tr>
<td>H$_2$N$-$Cl</td>
<td>10.44</td>
<td>9.85</td>
</tr>
<tr>
<td>F$_3$C$-$Cl</td>
<td>13.00</td>
<td>13.00</td>
</tr>
<tr>
<td>HOOC$-$Cl</td>
<td>12.13</td>
<td>...</td>
</tr>
</tbody>
</table>

*Reference 34.
*Reference 35.
*Reference 36.
*Reference 37.
*Reference 38.

To very strong (in fact FCl:NH$_3$ and HOCl:NH$_3$ complexes feature the strongest halogen bonding interactions among all complexes studied here) halogen bonding interaction (between the lone pair electrons of NH$_3$ and σ-hole of CIF and HOCl, respectively), lone pair orbital of NH$_3$ molecule is extraordinarily stabilized and that is why HOMO is not localized on the NH$_3$-end of the FCl:NH$_3$ and HOCl:NH$_3$ complexes anymore.

In order to prove the above argument, we have examined the neutral HOMO and the cationic LUMO $\beta$ (we note that LUMO $\beta$ exhibits similar density plot to cationic SONO) densities for FCl:NH$_3$ and HOCl:NH$_3$ complexes at different Cl···N halogen bond distances. Longer halogen bond distances are selected for this perusal in order to reduce halogen bond strengths. The respective halogen bond strengths and electron density critical points are also given in Figure 9. For all the configurations with varied halogen bond distances, the bond paths analyzed by AIM theory are linear and a bond critical point exists for all configurations, which are indicative of the existence of halogen bonding interaction in these complexes at the given halogen bond distance.

In the case of FCl:NH$_3$ complex, for the halogen bond distance longer than 2.72 Å (which is larger than the equilibrium distance 2.32 Å), the HOMO exhibits the lone pair orbital of NH$_3$. At this longer halogen bond distance, the halogen bonding interaction energy is reduced to 9.41 kcal/mol, as compared to the halogen bonding interaction energy of 11.29 at the equilibrium bond distance 2.32 Å. Similar result is also found for HOCl:NH$_3$ complexes, as shown in Figure 9. These results suggest that once the halogen bond interaction becomes weaker, the HOMO is essentially determined by the relative ionization energies of the two complex-forming moieties. In the case of FCl:NH$_3$ complex, as isolated NH$_3$ molecule possesses ionization energy lower than isolated CIF molecule, the HOMO features (which is the lone pair orbital of the NH$_3$ moiety) electron density localized on the NH$_3$-end of the complex. Furthermore, upon vertical ionization of this complex, the LUMO $\beta$ features that the charge migrates from the NH$_3$ moiety to the CIF moiety at the large halogen bond distance (2.72 Å). Similar charge migration is also found and discussed already for NCCI:NH$_3$ complex in this article.

Thus, the above distance-dependent change of the HOMO and LUMO $\beta$ density plots (Figure 9) corroborates the fact that halogen bond strength can have significant influence on the nature of charge migration in halogen bonded clusters following vertical ionization. On the same note, an interesting question can be raised: does charge migration stop above a certain halogen bond distance? We find that for FCl:NH$_3$ complex, the hole does not migrate anymore at Cl···N halogen bond distance longer than 2.72 Å. The respective halogen bond strengths and electron density critical points are also given in the figure.

FIG. 9. Canonical HOMO and LUMO $\beta$ of (a) FCl:NH$_3$ and (b) HOCl:NH$_3$ complexes, calculated at different halogen bond distances. The computation was performed at the wB97XD/6-31+G(d,p) level of theory.
bond distance of 4.32 Å. The hole density stays localized on the NH₃-end of this complex.

IV. SUMMARY AND CONCLUSIONS

The possibility to characterize electron correlation- and relaxation-driven processes and their controlling factors is attracting great interest nowadays, particularly due to contemporary development of the time-resolved spectroscopic technique using attosecond laser pulses. Continuing with this theme, in the present work, we have studied the ultrafast charge migration dynamics through unconventional halogen bonds. Furthermore, we have examined the controlling factors of charge migration through the halogen bonds. To the best of our knowledge, this is the first report in the literature that deals with the *ab initio* investigation of the ultrafast (sub-femtosecond) charge transfer dynamics through halogen bonds. In this work, we have presented molecular orbitals picture of the charge migration dynamics through this non-covalent bond.

To address ultrafast charge migration through halogen bonds following ionization of the representative halogen bonded cluster and their consequences and controlling factors, we have selected ACI:NH₃ complexes. Here, A represents F, OH, CN, NH₂, CF₃, and COOH substituents. The FCI:NH₃ complex exhibits the strongest Cl···N halogen bonding interaction and the H₂NCl:NH₃ complex features the weakest Cl···N halogen bonding interaction among all the complexes studied here.

The vertical ionization of a neutral halogen bonded complex produces a non-stationary electronic state which evolves in time at frozen nuclei VI point. Vertical ionization creates a localized hole in the complex. When the electron is removed from the HOMO, the initial hole is created at the HOMO orbital. However, the HOMO of the neutral complex is not a stationary orbital of the cation, and in order to time-propagate the hole density, the HOMO of the neutral complex is expressed as a linear combination of (stationary) molecular orbitals of the cation and time propagation of the hole density can be monitored by projecting the HOMO of the neutral on the stationary molecular orbitals of the cation at the fixed VI geometry of the complex. This procedure was first introduced by Levine and Remacle¹⁷a and we have closely followed their procedure to examine charge migration dynamics through halogen bonds in aforementioned halogen bonded clusters following their vertical ionization.

The key theoretical findings of this work are the following.

1. Upon vertical ionization of the halogen bonded NCCI···NH₃ complex, the hole migrates from the NH₃-end to the CICN-end of the halogen bonded NCCI···NH₃ complex at the VI point on the D₀ surface in approximately 0.5 fs. Similar (0.5-0.6 fs) time scale is also found for some other halogen bonded complexes, including NCCI:NH₃, H₂NCl:NH₃, F₃CCl:NH₃, and HOOCCI:NH₃.

2. On the contrary, two halogen bonded complexes, such as FCI:NH₃ and HOCl:NH₃, do not feature charge migration following vertical ionization to the D₀ cation state. These two complexes exhibit strongest halogen bonding interaction among all the halogen bonded complexes studied here.

3. Relative vertical ionization energies of CICN, CINH₂, CIF, ClOH, CIF₃, and ClCOOH with respect to that of NH₃ molecule and Cl···N halogen bond strength are found to play critical role in ultrafast charge migration through halogen bonds in the respective halogen bonded complexes.

4. It is argued in the recent literature²² that the KS-DFT method using B3LYP functional may fail to describe correctly the electron dynamics following ionization due to the presence of self-interaction error and absence of long range electron-electron interactions. However, our present work shows that B3LYP functional predicts results similar to that obtained with self-interaction-free DFT functionals, such as CAM-B3LYP, wB97XD, and M06HF.

5. Both the DFT and CASSCF levels of theory predict that the created hole charge density, following vertical ionization, favours formation of the hydrogen bond on the low-lying cationic potential energy surfaces of the halogen bonded complexes.

Understanding the charge migration dynamics through non-covalent bonds is of both fundamental and practical significance. In this work, for the first time, we have explored the time scale, consequences, and controlling factors of charge migration through an unconventional non-covalent bond, the halogen bond. Our next goal is to explore the same in other unusual non-covalent bonded systems, such as chalcogen, pnictogen, and tetrel bonded systems. From a broader perspective, the present work poses a number of questions: how sub-femtosecond charge migration affects the proceeding chemistry? Is it the time scale which controls subsequent chemical dynamics or is it the way charge is finally localized? These are very important questions in attosecond spectroscopy to be addressed in the near future. At this point, with the available computational and experimental results, it is difficult to address these questions fully. However, we see that there is a direct connection between the way charge is finally localized and the subsequent radical cationic reactivity. “Whether the attosecond time scale of charge migration has any impact on the proceeding chemistry?” is a question which is difficult to address immediately. Indeed, attosecond time scale addresses the fundamental time scale in which electron, nuclei, and light start to interact. This means that usual approximations, such as Born-Oppenheimer or the mean-field theories might be invalidated at this time scale. Many groups (including us) around the globe have started working to address these issues in greater detail. We hope that the systematic investigation presented in this paper will provoke others to think in this line in terms of non-covalent bonding interactions.

ACKNOWLEDGMENTS

This research was supported by the 12th Plan Grant of the Indian Institute of Science, Bangalore, India (Grant No. 12-0201-0243-01-403) and DST-SERB, India (Grant No. SB/S1/PC-50/2013). G.P. thanks UGC-FRP start-up grant for funding.
See supplementary material at http://dx.doi.org/10.1063/1.4922843 for ultrafast charge migration and subsequent reactivity in Cl···N halogen bonded clusters following vertical ionization.


A. D. Daniels, O. Farkas, J. B. Foresman, J. Cioslowski, and D. J. Fox, Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford CT, 2009.


A. D. Daniels, O. Farkas, J. B. Foresman, J. Cioslowski, and D. J. Fox, Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford CT, 2009.
