Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for Trapping of Gaseous Pollutants on Defective N-doped Graphene

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A. Structural Models

In single vacant sheet, nearest three carbon atoms of the vacant site have been substituted by nitrogen atoms (see Fig. 1(a,b)). This sheet named as SV-3N in the paper. In the other sheet, as shown in Fig.1 (c,d), a carbon dimer is removed (i.e. double vacancy, DV) and four carbon atoms which were covalently bonded with the dimer, are substituted by nitrogen atoms. This particular sheet is nomenclatured as DV-4N in this paper. Apart from these defective regions, other part of graphene remains in its pristine form. Note that, these two defect-sites are quite different in terms of pore area as well as nitrogen concentration.

B. Detail of Structures of SV-3N and DV-4N sheets

The equilibrium distances between any two nitrogen atoms at these SV (DV) sites are $\sim$ 2.6 Å-2.75Å ($\sim$ 2.7 Å-2.8 Å), quite larger than N-N single bond length ($\sim$ 1.47 Å). Thus, in these sheets, nitrogen atoms do not undergo reconstruction, forming homonuclear N - N covalent bonds. This is once again consistent with several experimental investigations, where X-ray photoelectron spectroscopy (XPS) spectra as well as scanning tunneling microscope (STM) imaging proves the absence of N-N bonds in the systems (Wang et. al. ACS Catal., 2012, 2, 781794). Further, the C-N distances in SV-3N and DV-4N appear as $\sim$ 1.32 Å-3.37Å and $\sim$ 1.33 Å-1.37 Å which are consistent with previous computational study by Yang-Xin Yu (Phys. Chem. Chem. Phys., 2013, 15, 16819 - 16827.).

Interestingly, the SV and DV defects are quite unstable in pristine graphene. In that case, two dangling bonds, appearing from half-filled sp^2 orbitals of under-coordinated carbon atoms at defect site, form stable C-C covalent bond. Consequently, as shown in different experimental as well as theoretical studies, these SV and DV defects get reconstructed to 5-9 and 5-8-5 defects, respectively (). However, SV-3N and DV-4N defects remain stable at ambient condition due to two major factors: (1) the stability of the lone pairs of electrons in the doped-N atoms and (2) unfavourable formation of weak homonuclear N-N bond(s) in possible reconstructed geometries (i.e. 5-9 or 5-8-5). In these sheets, N atoms of each pyridinic rings keep the lone pair of electrons in an sp^2 orbital, which remains in-plane with the system. As sp^2 orbitals of lone pairs are completely occupied, the defect sites become quite stable and less active towards reconstruction compared to the SV and DV in graphene. Moreover, due to the presence of these lone pairs, two N atoms repel each other electrostatically and avoid formation of the N-N bonds at defect-sites. Lower bond energy of N-N bond also reflects this fact and consequently justify the stability of these defects.(Stevenson, J. Am. Chem. Soc., 1955, 77, 2350 - 2350)

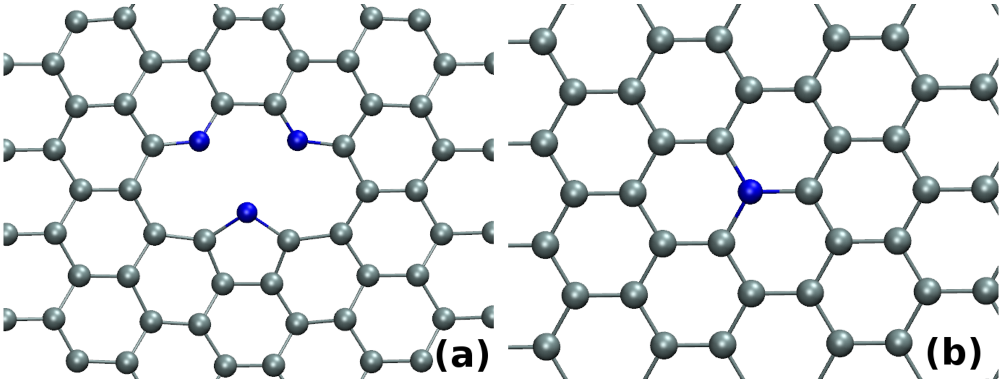

FIG. 1. Snapshots of (a) graphitic nitrogen and (b) pyrrolic nitrogen doped structures. Grey and blue colored balls depicts carbon and nitrogen, respectively.

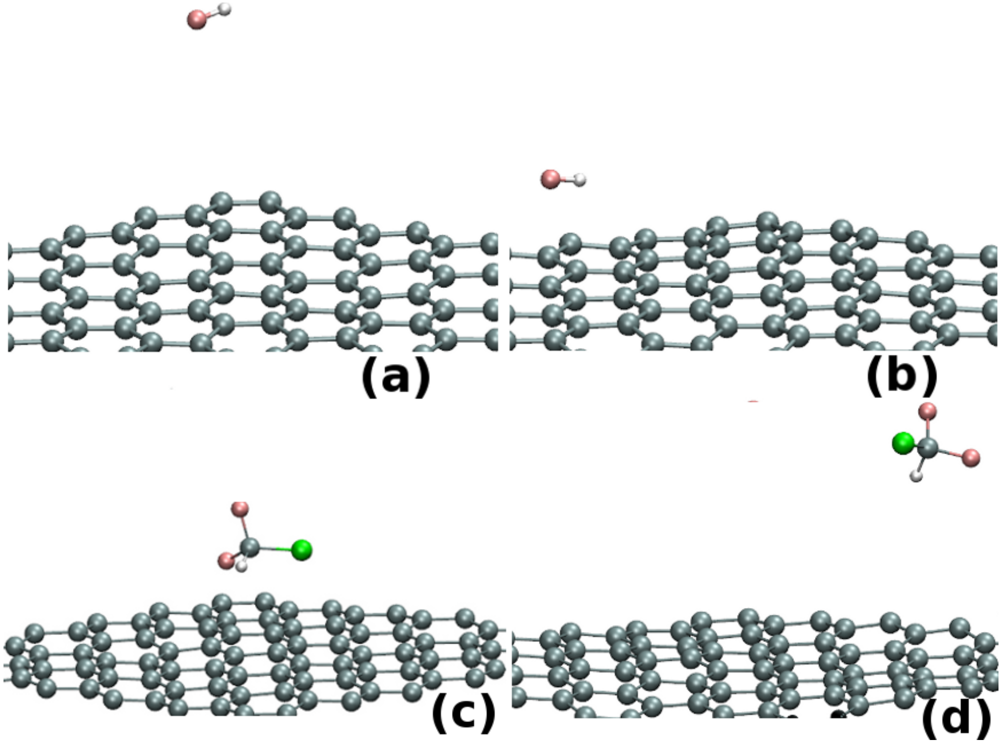

FIG. 2. Snapshots of (a,b) HF and (c,d) $CHClF_2$ on top of pristine graphene. BOMD simulations are performed in 300 K; snapshots are captured at (a,c) 0.5 ps and (b,d) 6 ps. White, pink and green colored balls represent hydrogen, fluorine and chlorine, respectively.

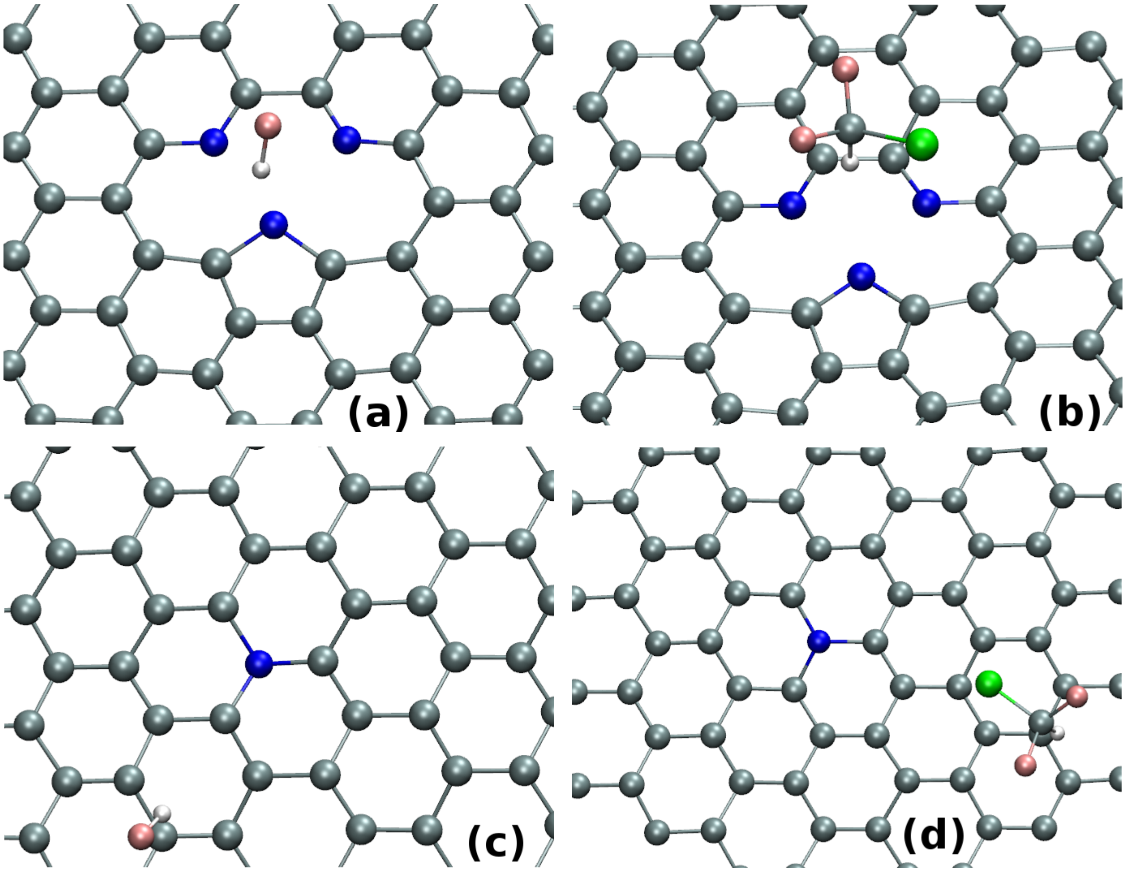

FIG. 3. Various snapshots of configurations of (a)HF and (b) $CHClF_2$ trapped on defect-site of pyrrolic nitrogen doped sheets after 10ps BOMD simulation are shown. Snapshots of (c) HF and ()$CHClF_2$ on graphitic nitrogen doped sheets after 10 are given.

C. Detail of DFT-based structures of SV-3N and DV-4N sheets with adsorbates

In its optimized geometry, as shown in earlier studies, two nitrogen of 3N-SV defect-site come out of the graphene plane by 0.16 Å but in the opposite directions (Muhich et. al. J. Phys. Chem. C, 2013, 117, 10523 - 10535). Furthermore, in presence of HF and HCN, SV-3N defect-site remains non-planar. As shown in Fig. 4 (a,b), N atom which is adjacent to HF remains out from the graphene plane by 0.3 Å and 0.15 Å, respectively. We named this particular out-of-plane shifted N atom as N_{out}. On this SV-3N defect site, H atom of HF and HCN remains directed towards N_{out}. As given in Table 1i (mail text), for HF (HCN), H atom stays much closer to N_{out} i.e. 1.66 Å (2.06 Å) away than the other two N atoms of the defect sites, where the N-H distances are 2.29 Å and 2.30 Å (2.23 Å and 2.26 Å). However, for $CHClF_2$ and CHF_3, as shown in Fig.4 (c,d), the H atom of molecules interacts with all the three N atoms almost identically. Here, the defect site remains almost planar,

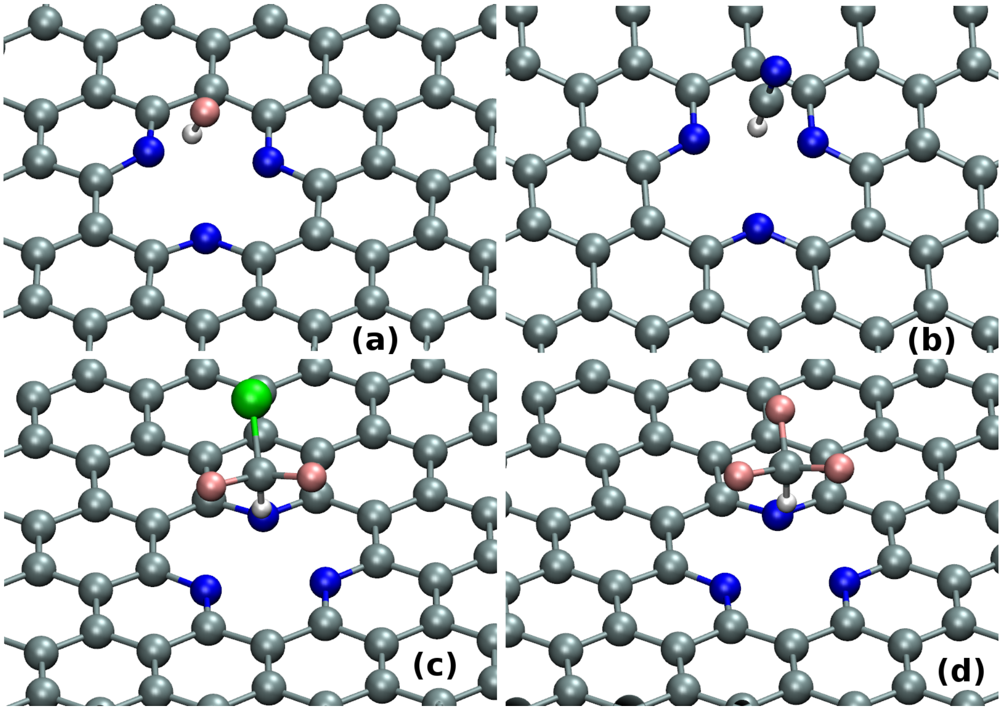

FIG. 4. DFT-based optimized structures of (a) HF (b) HCN (c) $CHClF_2$ and (d) CHF_3 on top of the defect-site of SV-3N.

where H of the molecule stays almost equidistant apart from all the three N of SV-3N. Now it's quite evident that linear molecules tend to be directed towards N_{out} due to formation of better electrostatic interaction between H and N_{out}. However, in case of $CHClF_2$ and CHF_3 trapped systems, this kind of directionality can cause repulsive interaction between Cl/F atom and graphene sheets. Thus, these molecules prefer to orient the H atom at the middle of the 3N-SV.

For DV, as shown in Fig. 5 (a-d), however, we do not find any prominent out-of-plane shift of N atoms for isolated as well as any of the gas-adsorbed systems. Apart from HF, H atom of other three molecules stay almost at the middle of the cavity and interact with all four nitrogen atoms identically. However, H of HF remains closer to two N atoms (2.00 Å and 2.06 Å) and far from other two (2.53 Å and 2.57 Å) (see Fig. 5 (a)).

D. Weak binding of $CHClF_2$ on SV-3N

To find out the the origin of the lower binding energy of CHClF2 on SV-3N, we look into the local structure of defect with and without the adsorbate molecule (i.e.$CHClF_2$).

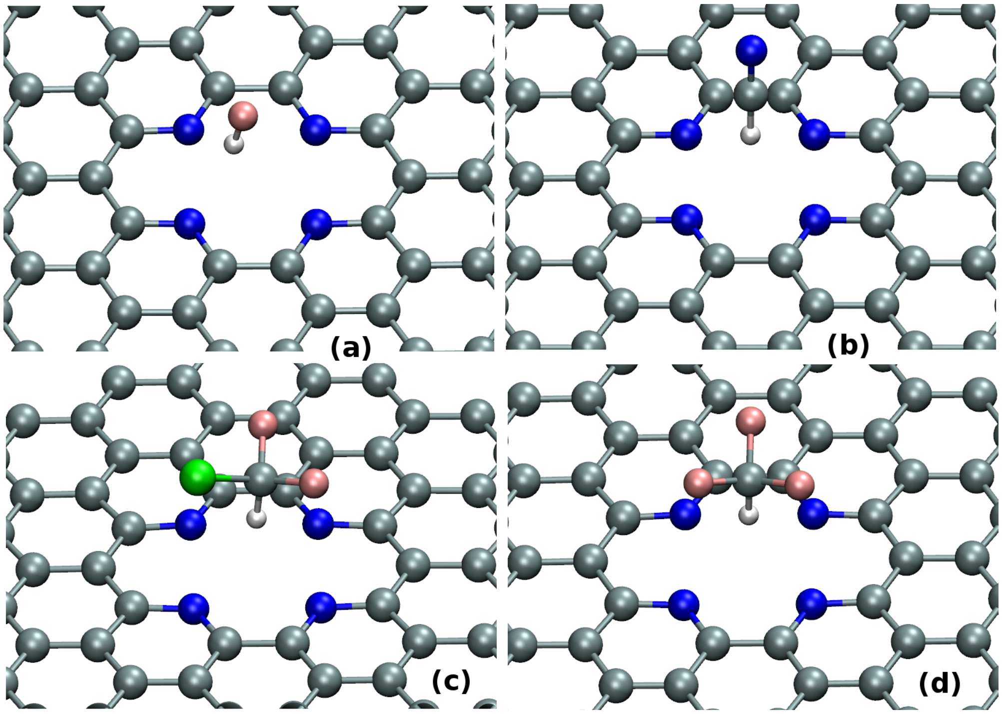

FIG. 5. DFT-based optimized structures of (a) HF (b) HCN (c) $CHClF_2$ and (d) CHF_3 on top of the defect-site of DV-4N.

As mentioned in the SI as well as other previous reports, without any adsorbate, due to the replusion among the lone-pair electrons of N at SV-site, one nitrogen atom moves out-of-plane by 0.16 Ang. And hydrogen atom of adsorbate molecules preferentially forms H -bond with that out-of-plane moved N atom. However, interestingly, unlike systems, the out-of-plane nitrogen atom gets pushed back in the cavity (out-of-plane distance reduce to 0.04 ang) as $CHClF_2$ binds with the defect-site. Repulsion between lone-pair electrons of Cl and that of N, results in this kind of geometric change. Now, as all three N atoms remain almost in-plane at the SV, the adsorbent remain in an unfavourable geometry. Thus, as a whole, the binding energy (i.e. the energy difference between ground state energy of adsorbate-adsorbent and individual adsorbate and adsorbent) of $CHClF_2$ on SV-3N appears to be quite lesser than other systems.

On the other hand, due to larger space in the cavity site, replusion among the lone-pair of nitrogen atoms, is not that prominent for DV-defect site compared to SV-defect. Thus, all the nitrogen atoms remain more or less in-plane for DV-4N with or without adsorbate molecules. Thus, in this case, adsorption of $CHClF_2$ does not create any unfavourable geometry of adsorbent. As a result, the binding energy of CHClF2 remains comparable to

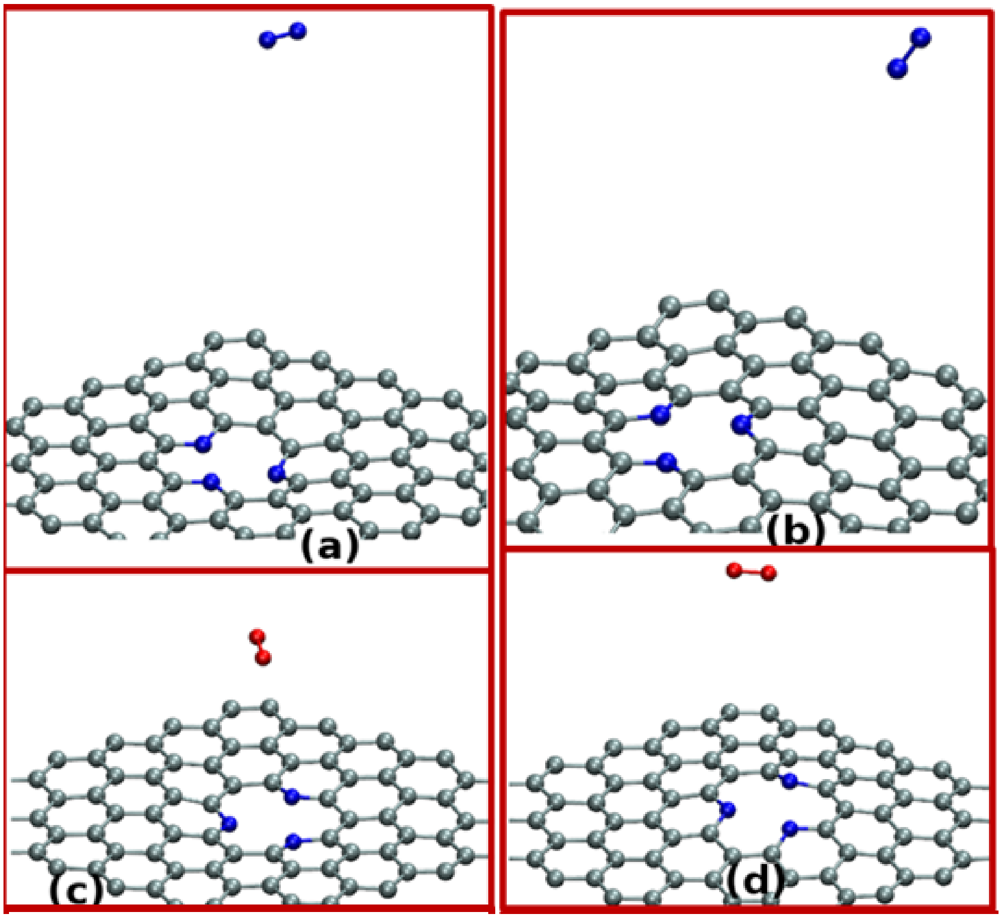

FIG. 6. Snapshots of configurations of N_2 and O_2 on SV-3N after (a,c) 0.5 ps and (b,d) 10 ps BOMD simulation.

that of HCN and CHF3 adsorbed systems.

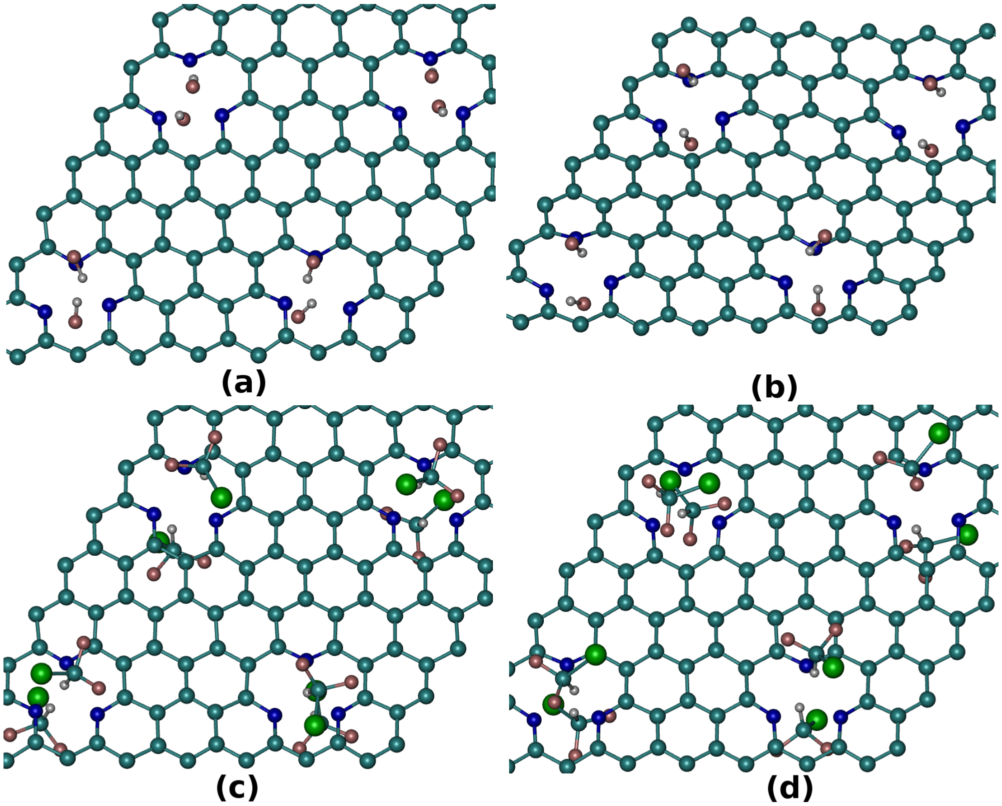

FIG. 7. Snapshots of configurations of HF on the both side of highly defect-dense SV-3N sheet after (a) 4 ps and (b) 8 ps BOMD simulation. On the same way, configuration of $CHClF_2$ on SV-3N after (c) 4ps and (d) 8ps simulation.

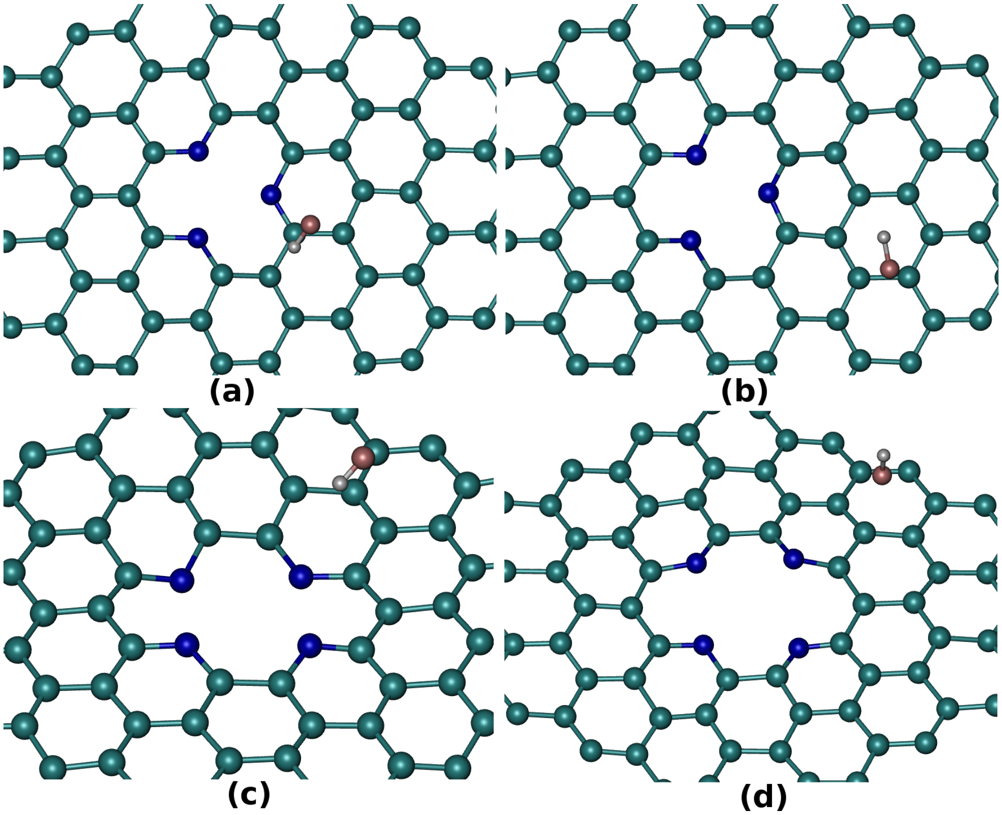

FIG. 8. Snapshots of configurations of HF on SV-3N at 600 K after (a) 4ps (b)4.2 ps and on DV-4N at 650 K after (c) 2ps (d) 2.1 ps BOMD simulations.