Theoretical Study on the New Types of Noble-gas Containing Neutral Molecules with Indolyl ring

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Abstract

We have been designing new types of molecules containing noble gas (Ng = Ar, Kr and Xe) atoms and cyclic functional groups. In the current study we used indole as a prototype of aromatic ring to design a novel noble gas molecule, FNg-$C_6H_4CCNH_3$. High-level electronic structure calculations have been performed to obtain the molecular structures and their stability. The results show moderate enhancement on the stability (2-5 kcal/mol) against the linear (three-body) dissociation by using the fused ring as compared to the pyrrole ring (FNg-C_4H_4N). Since both the bent and the linear dissociation barriers exceed 10 kcal/mol[1], these molecules are thus expected to be kinetically stable and might be found in future experiments at cryogenic conditions.

Motivation

In our previous research on aromatic noble-gas molecules, we found FNgC_4H_4N (FNg-Pyr)[2], (Ng = Ar, Kr, Xe) may be kinetically stable at low temperature. In the current study, we extend the aromatic group to a fused-ring functional group. In particular, we used the indole as the substituent to bond to the noble gas (FNg-Ind). The structures, stability, and the chemical bonding were studied using quantum chemical calculation.

Methods

Molecular structures, vibrational frequencies, and electron density were calculated using MP2 theory with the aug-cc-pVDZ basis set. CCSD(T)/aug-cc-pVTZ method was used obtain more accurate relative energies. For Ar the aug-cc-pV(D+*d*)Z basis sets were used, and for Xe the aug-cc-pVDZ-pp basis sets were used. Electronic structure calculations were performed by Gaussian 16 Rev. C01[3] programs. Electron density and contour plots of the calculated Laplace concentration were made using Multiwfn[4].

Results and Discussion

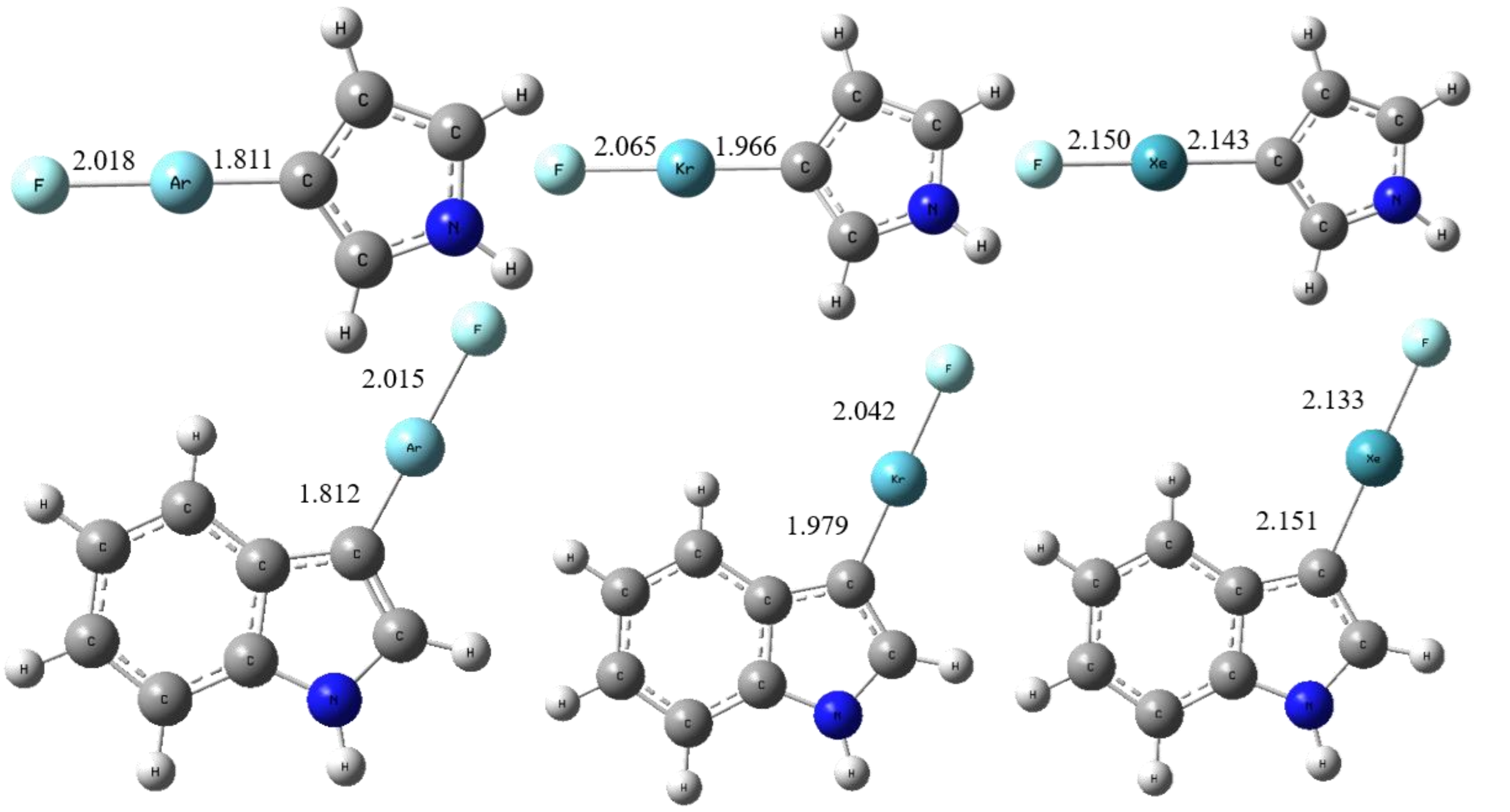

Figure 1. Calculated structures of 3-FNg-Pyr and 3-FNg-Ind with bond lengths in Å.

Structure: Figure 1 shows the structures of 3-FNg-Pyr and 3-FNg-Ind. All structures are planar. As the size of Ng (Ar–Xe) increases, the bond lengths on the organic aromatic ring do not show significant changes, while the Ng-F and C-Ng bond lengths also increase significantly (0.1-0.2 Å). The F-Ng-C bond angles are close to 180 degrees.

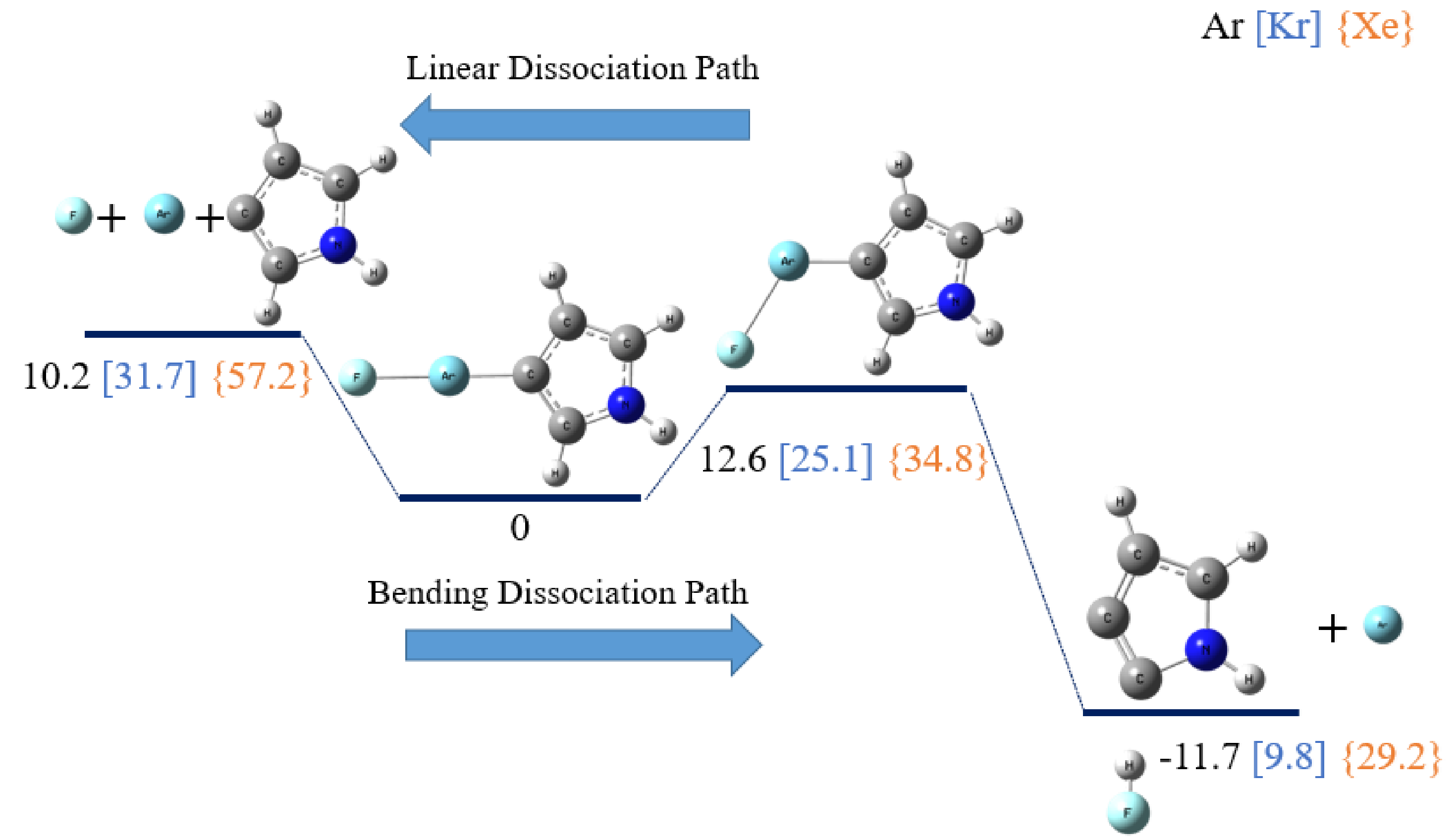

Figure 2. The calculated potential energy (kcal/mol) profile of 3-FNg-Pyr (Ng =Ar, Kr and Xe) for linear and bending dissociation pathway.

Stability: The stability of noble-gas molecules depends on the energy barrier of the dissociation pathways. Figure 3 shows both the linear and bending dissociation pathways of FNg-Ind. The linear dissociation pathway follows a three-body dissociation mechanism. For FNg-Ind, there are two bending dissociation pathways: one proceeds via TS1, which abstracts a hydrogen from the pyrrole ring, while the other proceeds via TS2, which abstracts a hydrogen from the benzene ring. The predicted linear dissociation energy for 3-FAr–py is approximately 10.2 kcal/mol. By fusing a benzene ring, the linear dissociation energy increases by 2–5 kcal/mol. We also attempted to fuse a benzene ring at a different position on pyrrole to form an isoindole structure, but it was found to be unstable. We have also tried to attach the noble gas atom at the other position on the pyrrole ring, but the linear dissociation stability were found to be 4.3 kcal/mol lower. The bending dissociation barrier does not change significantly upon ring modification. Additionally, we predict that substituting hydrogen with fluorine at 2 and 4 position could increase the bending dissociation barrier by 3.0 kcal/mol.

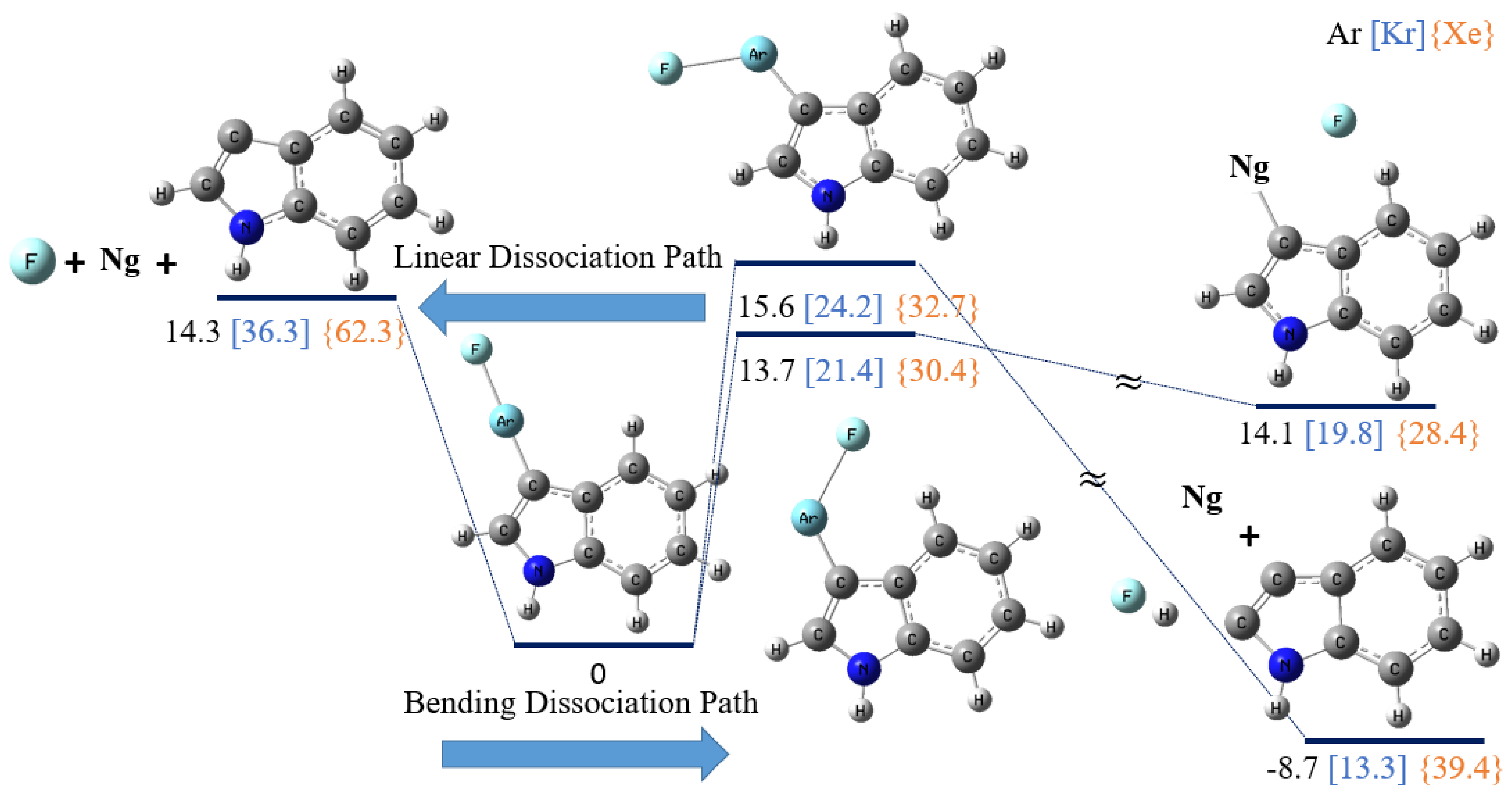

Figure 3. The calculated potential energy profile of 3-FNg-Ind (Ng =Ar, Kr and Xe) for linear and bending dissociation pathway. The energy in kcal/mole and frequency in cm^{-1}.

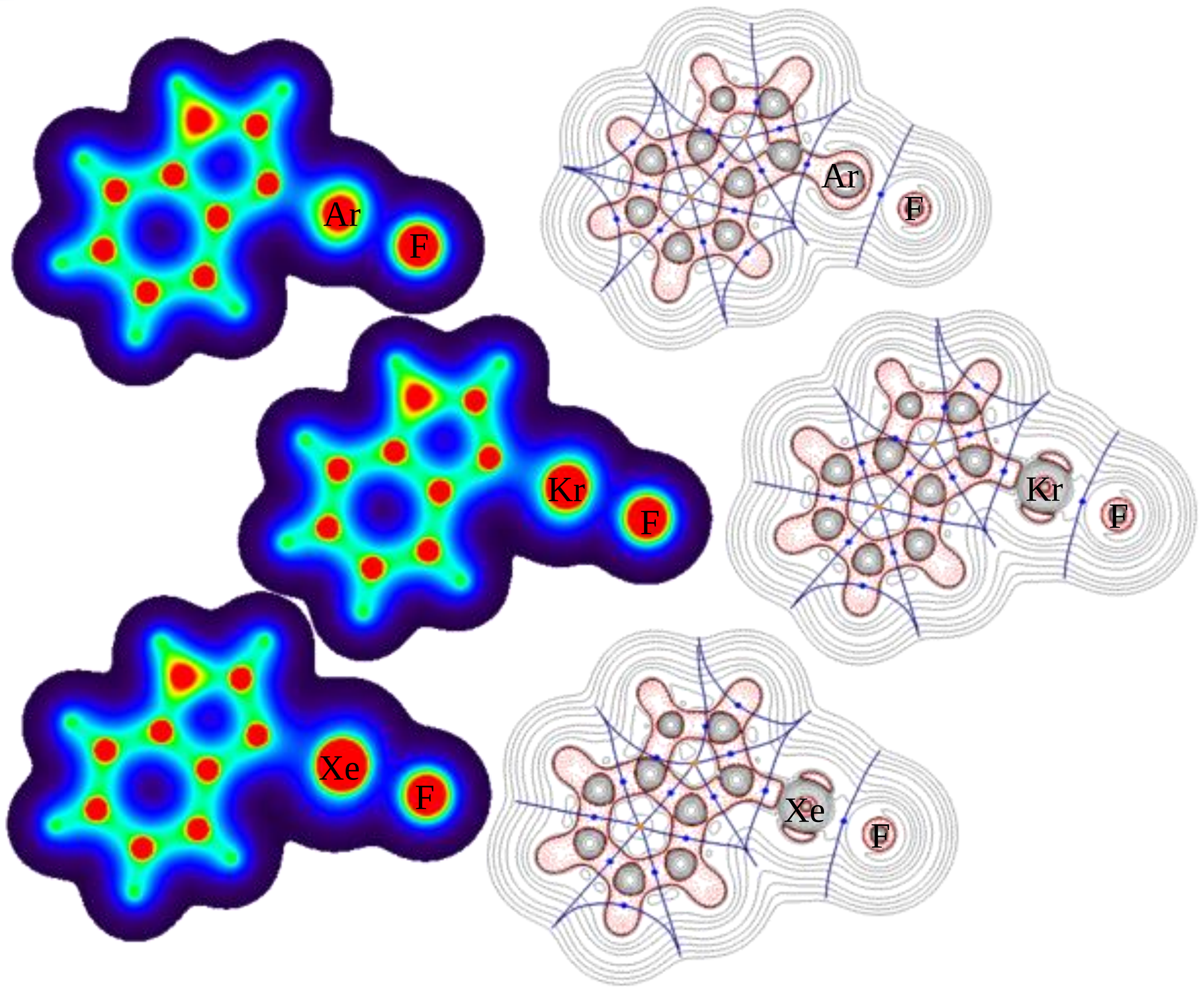

Figure 4. Electron density maps and Laplacian analysis of 3-FNg-Ind (Ng =Ar, Kr and Xe).

Electron Density Maps and Laplacian: The Ng–F bond exhibits low electron density, indicating an ionic-like interaction, whereas the C–Ng bond shows higher electron concentration, suggesting partial covalent character. Laplacian maps further confirm this contrast in electron localization: blue contour lines represent electron depletion associated with ionic or nonbonding regions, while red contours indicate electron accumulation, characteristic of covalent bonding.

Conclusion

In this study, we examine the structure of 3-FNg-Ind. Compared to 3-FNg-Pyr, the linear dissociation energy increases by approximately 2–5 kcal/mol, indicating that fusing a benzene ring enhances the molecule's stability.

Most of the energy required for the linear and bending dissociation is higher enough to avoid 3-FNg-Ind easily dissociated (> 10 kcal/mole). So we expect that the nobles gas molecule contain Indolyl ring are observable at low temperature.

References

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