Theoretical Study of FNg-CH=CH-NH_2 (Ng = Ar, Kr, Xe), a Set of Potentially Stable Noble Gas-Containing Molecules

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Abstract

In the current study, we investigate the noble-gas (Ng) containing molecules of the type: FNg–CH=CH–NH_2 where Ng can be Ar, Kr or Xe atom. The molecular structures, energies and their unimolecular dissociation pathways are calculated by high-level electronic structure calculation. The results indicate that for Ng = Ar, the linear dissociation energy (~6.9 kcal/mol) is slightly below the kinetic stability threshold [1], whereas the Kr- and Xe-containing analogues exhibit significantly higher stability. These results suggest that this molecular class may constitute a series of kinetically stable molecules and might be found or synthesized in future experiments at cryogenic conditions.

Motivation

Noble-gas chemistry has long been regarded metastable species since Ng elements possess closed-shell electronic configurations and exhibit extremely high ionization energies under normal conditions. However, in 1962, Bartlett synthesized the first noble gas-containing molecules Xenon Hexafluoroplatinate ($XePtF_6$) [2], which experimentally demonstrating that noble gas atom can participate in chemical bonding when interacting with sufficiently strong oxidants.

In the previous theoretical studies about aromatic noble-gas molecules, FNg-C_4H_4N (FNg-Pyrrole) (Ng= Ar, Kr, Xe) [3] , have been found to be kinetically stable under low temperature. Motivated by these findings and building upon prior investigations of aromatic Ng species, we designed this type of molecule, which contains a subset of functional groups, in this research.

Methods

Geometry optimizations were performed using second-order Møller–Plesset perturbation theory (MP2) with Dunning's correlation-consistent aug-cc-pVDZ basis sets. Additional calculations employing the MPW1B95 density functional with aug-cc-pVDZ and aug-cc-pVTZ basis sets were carried out for comparison.

More accurate relative energies were obtained from single-point CCSD(T)/aug-cc-pVTZ high-level calculations on the optimized structures. For Ar atoms, aug-cc-pV(D+d)Z and aug-cc-pV(T+d)Z basis sets were used, while Xe atoms were described using aug-cc-pVDZ-pp and aug-cc-pVTZ-pp basis sets with relativistic pseudopotentials. All electronic structure calculations were performed with Gaussian 16 Rev. C.01[4]. Electron density and Laplacian analyses were conducted using Multiwfn [5].

Results and Discussion

1. Structure

The F–Ng bond distances systematically increase with the atomic number of the noble gas atom, consistent with the enlargement of atomic size. From Ar to Kr, the F–Ng bond length increases by approximately 0.150 Å (MP2) and 0.135 Å (MPW1B95), while a larger increment of about 0.170 Å (MP2) and 0.165 Å (MPW1B95) is observed from Kr to Xe. In contrast, the Ng–C bond lengths show only minor variations, with changes limited to approximately 0.12 Å (MP2) and 0.11 Å (MPW1B95).

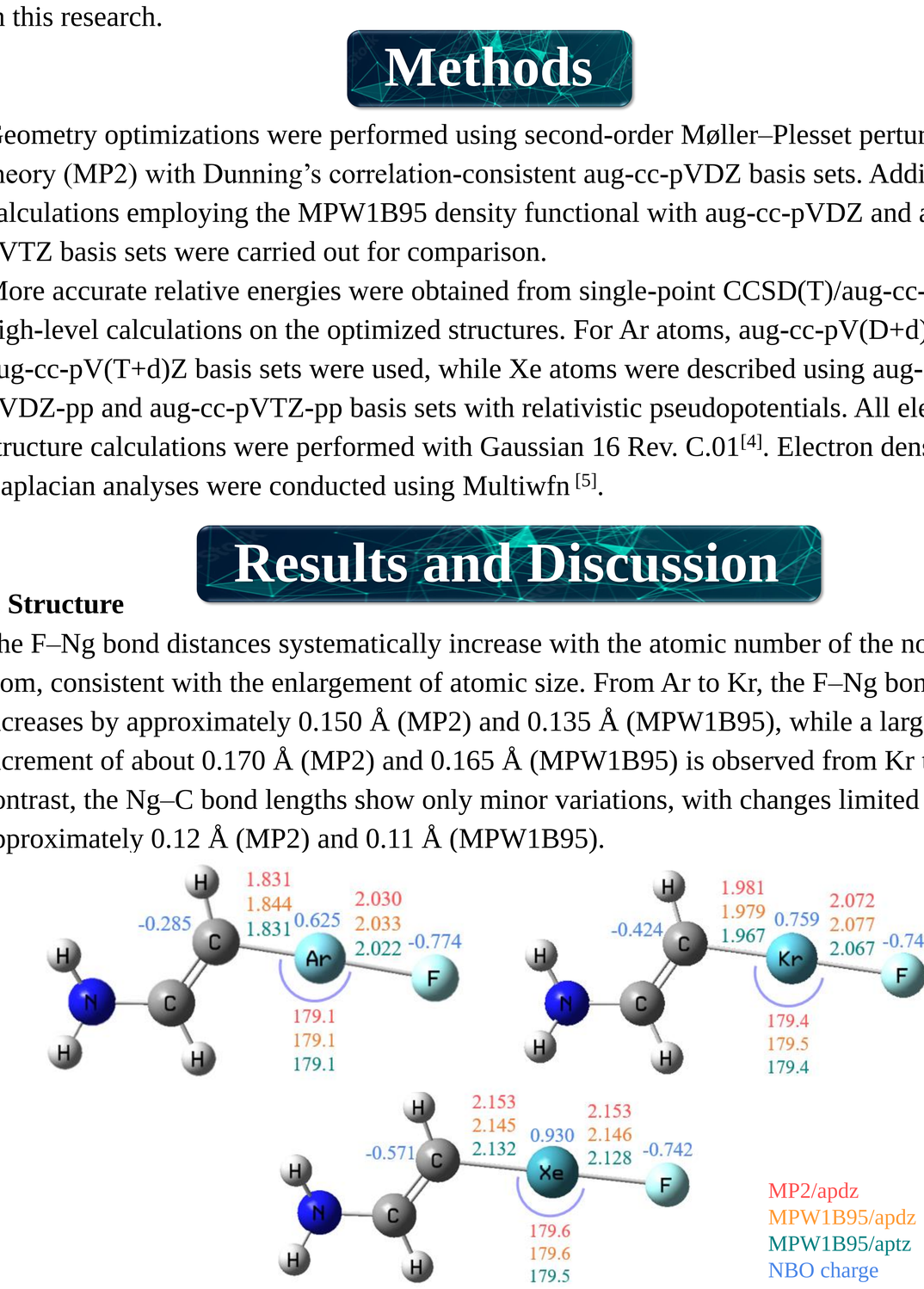

Figure 1. Optimized bond lengths, bond angles and NBO Charges of FNg-CH=CH-NH_2 (Ng = Ar, Kr, Xe). The unit of bond length is Å and bond angle is degree.

2. Energy and Stability

Molecular stability was evaluated by analyzing the energy barriers of linear and bending dissociation pathways. Two distinct transition states (TS) were identified for the bending mechanism, both leading to HF elimination identical final products, but differing in the hydrogen-shift: one abstracts H from the carbon adjacent to –NH_2 group, whereas the other involves the terminal carbon.

For all Ng atoms (Ar, Kr, Xe), hydrogen transfer from the nitrogen-adjacent carbon consistently exhibits a lower barrier by approximately 5~6 kcal/mol, indicating that Pathway 2 is kinetically favored over Pathway 3. The preference likely arises from electronic stabilization provided by the –NH_2 group along the reaction coordinate.

For Ng = Ar, the linear dissociation barrier (Pathway 1) (6.9 kcal/mol) lies slightly below the kinetic stability threshold, whereas the bending barriers (12.1 and 17.8 kcal/mol), satisfying the stability criterion. Substitution with Kr or Xe significantly increases all the barriers, reflecting enhanced kinetic stability with increasing Ng polarizability.

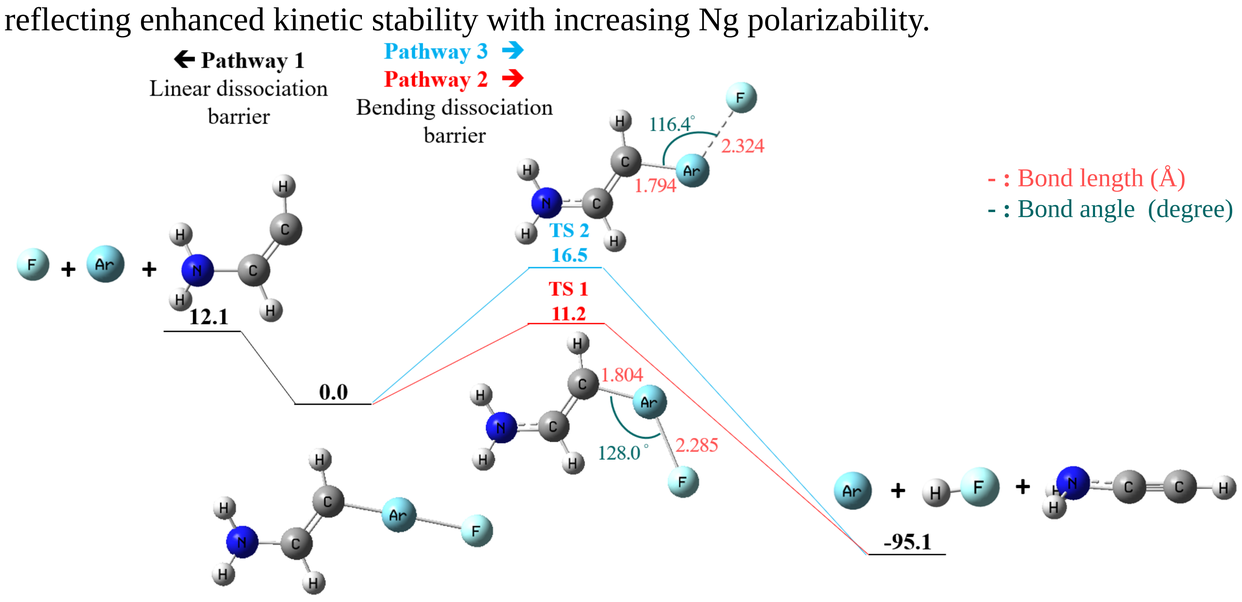

Figure 2. Reaction pathways, relative energies and representative TS geometries of FNg-CH=CH-NH_2. (Taking Ng=Ar at MP2/apdz level as an example.)

Table 1. Calculated relative energy and barriers of FNg-CH=CH-NH_2. (Unit: kcal/mol)

Dissociation path	FNg-CH=CH-NH_2		
	Ng = Ar	Ng = Kr	Ng = Xe
Pathway 1	12.1 , 12.1 , 6.9	32.4 , 28.3 , 27.0	57.9 , 50.8 , 51.5
Pathway 2	11.2 , 12.6 , 12.1	20.3 , 20.1, 20.0	30.8 , 29.3 , 29.2
Pathway 3	16.5 , 19.3 , 17.8	25.6 , 26.3 , 25.6	35.2 , 34.2 , 33.8

- :MP2/apdz
- :MPW1B95/aptz
- :CCSD(T)/aptz//MP2/apdz

3. Electron Density Distribution

As shown in Figures 1 and 3, the negative charge is predominantly localized on the F atom for all systems examined (Ng = Ar, Kr, Xe). The calculated charge separation between F and Ng is significantly larger than that between Ng and C. The calculated charge separation between F and Ng is consistently larger than that between Ng and C for all noble-gas atoms examined (Ar, Kr, Xe). This asymmetric distribution indicates greater electron density localization within the Ng–C interaction, consistent with partial covalent character, whereas the F–Ng bond exhibits more pronounced charge separation, suggesting a predominantly ionic interaction governed by electrostatic attractive forces.

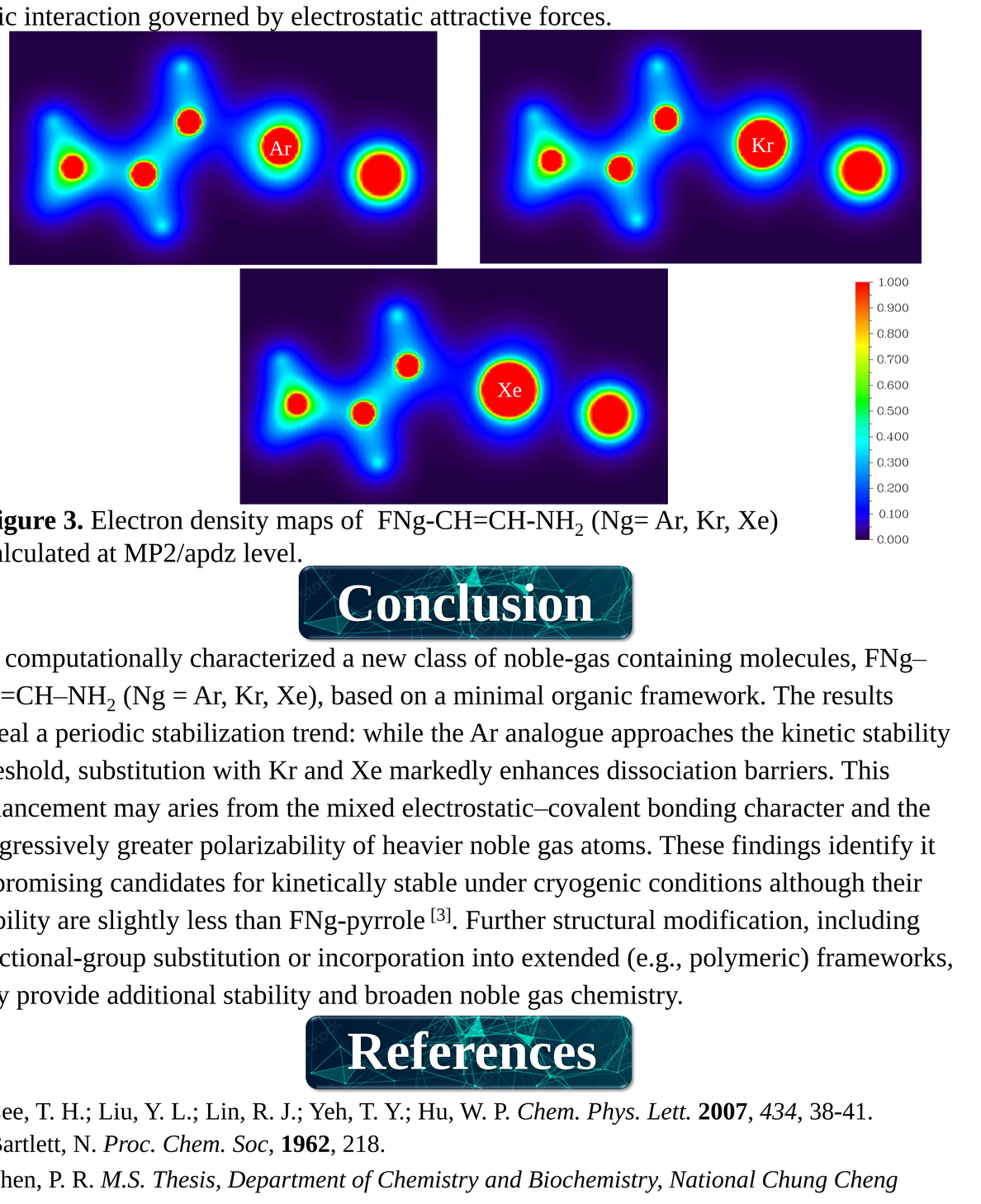

Figure 3. Electron density maps of FNg-CH=CH-NH_2 (Ng= Ar, Kr, Xe) calculated at MP2/apdz level.

Conclusion

We computationally characterized a new class of noble-gas containing molecules, FNg–CH=CH–NH_2 (Ng = Ar, Kr, Xe), based on a minimal organic framework. The results reveal a periodic stabilization trend: while the Ar analogue approaches the kinetic stability threshold, substitution with Kr and Xe markedly enhances dissociation barriers. This enhancement may aries from the mixed electrostatic–covalent bonding character and the progressively greater polarizability of heavier noble gas atoms. These findings identify it as promising candidates for kinetically stable under cryogenic conditions although their stability are slightly less than FNg-pyrrole [3]. Further structural modification, including functional-group substitution or incorporation into extended (e.g., polymeric) frameworks, may provide additional stability and broaden noble gas chemistry.

References

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