Noble Gas Compounds

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Is it Possible To Synthesize a Neutral Noble Gas Compound Containing a Ng–Ng Bond? A Theoretical Study of H–Ng–Ng–F (Ng = Ar, Kr, Xe)[**]

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Since the discovery of the noble gases in 1904 by Ramsey, chemists have taken up the challenge to overcome the reluctance of the Group 8 elements to form chemical bonds. The story of the decade-long failures and the circumstances which eventually led to the first syntheses of noble gas compounds by Bartlett[1] and Hoppe[2] is a fascinating example of the endurance and the creativity of great chemists who were determined to overcome the obstacles posed by nature.[3] A large number of noble gas compounds have since been isolated in the condensed phase; however, until recently only molecules of xenon and krypton were chemically synthesized, because chemical inertness increases with decreasing atomic number of the noble gas (Ng) atom. The first chemically bonded neutral argon compound, HArF, was not prepared until 2000 by Khriachtchev et al.[4] The molecule was synthesized by photolyzing HF in an argon matrix at low temperature, and it was identified by comparing its vibrational spectrum with those obtained from quantum chemical calculations. HArF is only stable as a matrix-isolated species, and thus it is not a genuine "bottleable" compound. Salt compounds of ArF^+ have been predicted to be isolable in principle because the calculated bond dissociation energy of the cation is very high (49 $kcal\,mol^{-1}$).[5] To date the search for weakly coordinating anions which stabilize ArF^+ has not been successful and remains a challenge for experimentalists. Theoretical studies have shown that the outlook for synthesizing neutral compounds with actual chemical bonds similar to helium and neon homologues is not very bright.[6]

Another challenge posed by noble gas chemistry is the synthesis of a compound which contains two noble gas atoms that are connected by a chemical bond Ng–Ng. In 1997, Seppelt succeeded in isolating a salt with the cation Xe_2^+ that has a Xe–Xe bond with an interatomic distance of 3.087(1) Å.[7] A neutral compound having a Ng–Ng bond seems highly unlikely because two noble gas atoms with a filled valence shell should not engage in chemical bonding with each other. On the other hand, we learned from the ground-breaking work of Khriachtchev et al.[4] that the cooperative effect of hydrogen and fluorine atoms bonded at opposite sides of a noble gas atom induces a strongly covalent bond between hydrogen and argon and a dominantly ionic bond between HAr^+ and F^-.[8] It seemed plausible to us that the synchronous influence of hydrogen and fluorine might even be substantial enough to induce chemical bonding between noble gas atoms in HNgNgF. Herein we report quantum chemical calculations[9] of the latter species, where Ng = Xe, Kr, and Ar. We also present the calculated reaction pathways and activation energy for the decomposition of HNgNgF.

Figure 1 shows the optimized geometries of the calculated equilibrium structures and the transition states. All tetraatomic species HNgNgF are minima on the potential energy surface (PES) with a linear ($C_{\infty v}$) geometry calculated using DFT at the m05-2x/def2-TZVPP level.[10] Reoptimization using MP2/def2-TZVPP and CCSD(T)/aug-cc-pVTZ also gave linear energy minima for HArArF and HXeXeF.[11] Note that values predicted with m05-2x/def2-TZVPP for the Ar–Ar and Xe–Xe bonds are very similar to the values using CCSD(T)/aug-cc-pVTZ. The theoretical prediction for the Xe–Xe bond length in HXeXeF is close to the experimental and the calculated Xe–Xe distance in the Xe_2^+. The value for $r(Xe{-}Xe)^+$ obtained using CCSD(T)/aug-cc-pVTZ and MP2/def2-TZVPP is 3.107 Å and 3.078 Å, respectively.

Figure 2 shows the theoretically predicted reaction coordinates for the decomposition of HNgNgF yielding HF and 2Ng as the most stable final products. The decomposition pathway of HNgNgF initially leads to the triatomic species HNgF, and Ng via hydrogen migration. The IRC calculations, which use TS1 as the starting point, yield weakly bonded van der Waals complexes HNgF···Ng, which are only slightly lower in energy than the separated species. The calculations using CCSD(T)/aug-cc-pVTZ predict that the noble gas compounds HNgF decompose to HF and free Ng via TS2, with activation barriers between 23.7 $kcal\,mol^{-1}$ (HArF) and 39.2 $kcal\,mol^{-1}$ (HXeF). The theoretical values are in good agreement with previous calculations.[12]

The most important results, which are shown in Figure 2 are the calculated activation barriers TS1 for the reaction HNgNgF → HNgF···Ng. The ab initio calculations suggest that HArArF is only a very shallow energy minimum on the PES. The barrier for the decomposition using CCSD(T)/aug-cc-pVTZ and MP2/def2-TZVPP is 1.4 $kcal\,mol^{-1}$ and 0.1 $kcal\,mol^{-1}$, respectively. The zero-point energy (ZPE) corrections slightly increase the barrier to 1.6 $kcal\,mol^{-1}$ at the CCSD(T)/aug-cc-pVTZ level and 0.2 $kcal\,mol^{-1}$ at the MP2/def2-TZVPP level. The calculated barrier using m05-2x/def2-TZVPP is also quite small (0.2 $kcal\,mol^{-1}$, which increases to 0.3 $kcal\,mol^{-1}$ with ZPE corrections). These results are in good agreement with the ab initio calculations. It seems highly unlikely that HArArF can be observed experimentally. The

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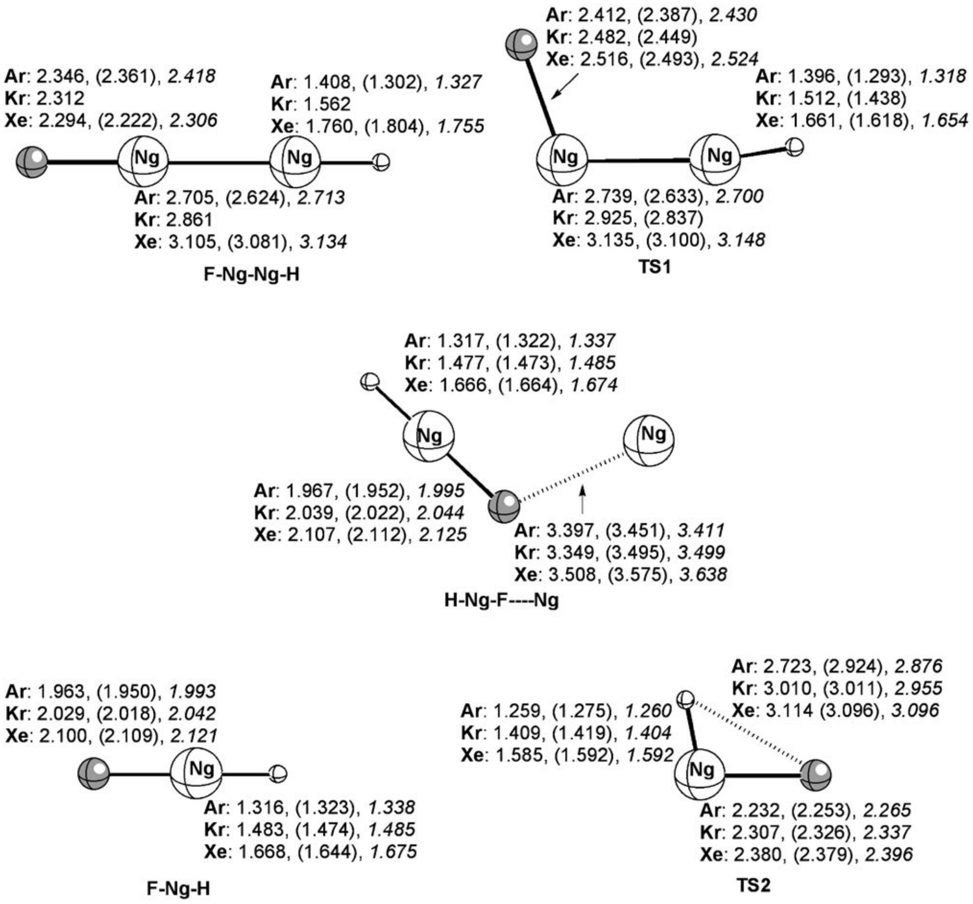

Figure 1. Optimized geometries of the stationary points and transition states of the decomposition pathways. Bond distances are given in Å. The first, second (in parentheses), and the third (italicized) value for each bond distance is calculated at the m05-2x/def2-TZVPP, MP2/def2-TZVPP, and CCSD(T)/aug-cc-pVTZ levels, respectively.

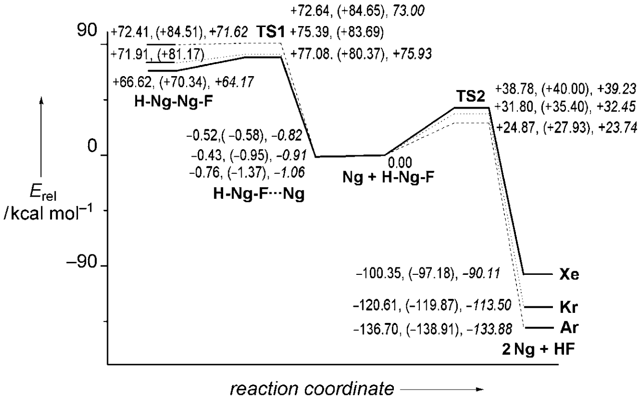

Figure 2. Calculated reaction coordinates for the decomposition of HNgNgF (Ng = Ar, Kr, Xe). The first value gives the relative energies (in kcal mol^{-1}) at m05-2x/def2-TZVPP + ΔZPVE. The second value in parentheses is calculated using MP2/def2-TZVPP, and the third value in italics is calculated using CCSD(T)/aug-cc-pVTZ.

calculations predict a similar situation for the heavier homologue HKrKrF. Single-point energy calculations at the MP2/def2-TZVPP//m05-2x/def2-TZVPP level,[11] predict a barrier of 2.5 kcal mol^{-1}. A slightly higher barrier of 4.1 kcal mol^{-1} is calculated at the m05-2x/def2-TZVPP level and (3.5 kcal mol^{-1} with ZPE correction). These values might be too low to make HKrKrF a viable compound.

The situation, however, looks different for the xenon homologue HXeXeF. The calculated activation barrier TS1 is 11.8 kcal mol^{-1} using CCSD(T)/aug-cc-pVTZ and 10.0 kcal mol^{-1} using MP2/def2-TZVPP. The barrier becomes slightly higher when ZPE corrections are considered reaching 13.1 kcal mol^{-1} at the CCSD(T)/aug-cc-pVTZ level at the 11.1 kcal mol^{-1} and MP2/def2-TZVPP level. The value using m05-2x/def2-TZVPP for the barrier is 9.5 kcal mol^{-1} (10.5 kcal mol^{-1} with ZPE corrections), which is in agreement with the ab initio values. The substantial activation barrier, which is predicted at different levels of theory, suggests that HXeXeF could be observed in a low-temperature xenon matrix.[13]

It should be relatively easy to identify HXeXeF by its IR spectrum, which according to the calculations is clearly different from the IR spectrum of HXeF. To our knowledge, there is no report which presents the experimental observation of HXeF, which should be prepared along with HXeXeF during photolysis of HF in a xenon matrix. Table 1 shows the theoretically predicted vibrational frequencies and IR intensities of both compounds using m05-2x/def2-TZVPP. There are two vibrational modes of HXeF and HXeXeF that have a very large intensity in the infrared spectrum. For HXeF, the IR-active Xe–F stretching mode is predicted at 468 cm^{-1} and the Xe–H stretching mode is calculated at 2141 cm^{-1}. The strongly IR-active modes of HXeXeF are calculated at 1352 cm^{-1} (Xe–F), whereas the Xe–H stretching mode is predicted at 312 cm^{-1}. The absolute values for the harmonic vibrations are probably too large, but the two xenon compounds can still be identified by the large shift of about 800 cm^{-1} for the Xe–H stretching mode. Table 1 gives also the calculated vibrational frequencies and IR intensities for the argon compounds HArF and HArArF, and for the krypton species HKrF and HKrKrF. The experimentally observed frequencies for HArF[4] and HKrF[14] suggest that the theoretical values for the vibrational frequencies are larger by about 10 %.

Table 1: Calculated IR frequencies (cm^{-1}) and intensities (km mol^{-1}) at m05-2x/def2-TZVPP with experimental values given in parentheses.

Frequency	Intensity	Mode	Frequency	Intensity	Mode
H-Ar-Ar-F			**H-Ar-F**		
68.0[a]	1.0	F-Ar-Ar bend	472.1 (*435.7*)[b]	221.1	Ar-F stretch
159.7	41.7	Ar-Ar stretch	716.2[a] (*686.9*)[b]	27.2	bend
317.3	104.4	H-Ar-Ar bend	2114.9 (*1965.7–1972.3*)[b]	439.2	Ar-H stretch
384.5	34.5	Ar-F stretch			
1676.6	8804.1	Ar-H stretch			
H-Kr-Kr-F			**H-Kr-F**		
72.9	7.3	F-Kr-Kr bend	457.4 (*414.2–417.0*)[c]	206.1	Kr-F stretch
135.6	38.4	Kr-Kr stretch	645.3^{a} (*645.9-650.9*)[c]	8.4	bend
304.0	253.3	H-Kr-Kr bend	2076.4 (*1925.4–1951.6*)[c]	378.1	Kr-H stretch
616.1[a]	18.0	Kr-F stretch			
1692.4	5878.4	Kr-H stretch			
H-Xe-Xe-F			**H-Xe-F**		
20.2[a]	7.5	F-Xe-Xe bend	467.9	206.4	Xe-F stretch
126.3	30.3	Xe-Xe stretch	643.6[a]	0.3	bend
296.0[a]	4.4	H-Xe-Xe bend	2140.5	276.1	Xe-H stretch
311.9	522.6	Xe-F stretch			
1351.5	3808.8	Xe-H stretch			

[a] Degenerate mode. [b] Reference [4b]. [c] Reference [12].

We analyzed the electronic structure of the noble gas compounds to understand the nature of the chemical bonding. Table 2 shows the calculated atomic partial charges of HNgNgF and HNgF. The fluorine atom always carries a large negative charge, which is close to −1. The negative charge on the fluorine atom in HNgNgF is even larger than in the respective HNgF molecule. The charge distribution suggests that the tetraatomic species may be described as HNgNg^{+} cations, which are electrostatically bonded to F^{-}. The noble gas atoms are positively charged. Note that the Ng atom that is bonded to the fluorine atom is always less positive compared to the Ng atom that is bonded to hydrogen atom. Another interesting result is the partial charge of the hydrogen atom in HXeXeF, which is essentially neutral.

Table 2: NBO Charges of HNgNgF and HNgF at the MP2/def2-TZVPP//MP2/def2-TZVPP level.

	Ar	Kr	Xe
H-Ng1-Ng2-F[a]	q(H) = 0.42	q(H) = 0.30	q(H) = −0.01
	q(Ng1) = 0.51	q(Ng1) = 0.43	q(Ng1) = 0.59
	q(Ng2) = 0.05	q(Ng2) = 0.16	q(Ng2) = 0.32
	q(F) = −0.98	q(F) = −0.88	q(F) = −0.91
H-Ng-F	q(H) = 0.26	q(H) = 0.12	q(H) = −0.04
	q(Ng) = 0.59	q(Ng) = 0.71	q(Ng) = 0.87
	q(F) = −0.84	q(F) = −0.83	q(F) = −0.83

[a] Using m05-2x/def2-TZVPP optimized geometry for Ng = Kr.

Figure 3 shows the contour line diagrams of the Laplacian distribution $\nabla^2\rho(r)$ of HNgNgF and HNgF. The results of the atom in molecules (AIM)[15] calculations are given in Table 3. The shape of the Laplacian distribution indicates the nature of the bonding interactions. The fluorine atom in all the compounds has a spherically symmetrical Laplacian distribution, which underscores the classification of a fluoride F^{-} anion. The Ar–H bonds in HArArF and HArF possess an area of continuous charge concentration $\nabla^2\rho(r) > 0$ (solid lines), which suggest an ArH^{+} moiety. The Laplacian distribution of the second argon atom in HArArF is nearly undistorted which agrees with the very low energy that is necessary to change the linear equilibrium structure to TS1. The electronic charge at hydrogen in the krypton and xenon compounds is higher than those in the argon compounds (see the atomic partial charges in Table 2). This difference is apparent from inspection of the area of charge concentration in the Kr–H and Xe–H moieties, which becomes more shifted

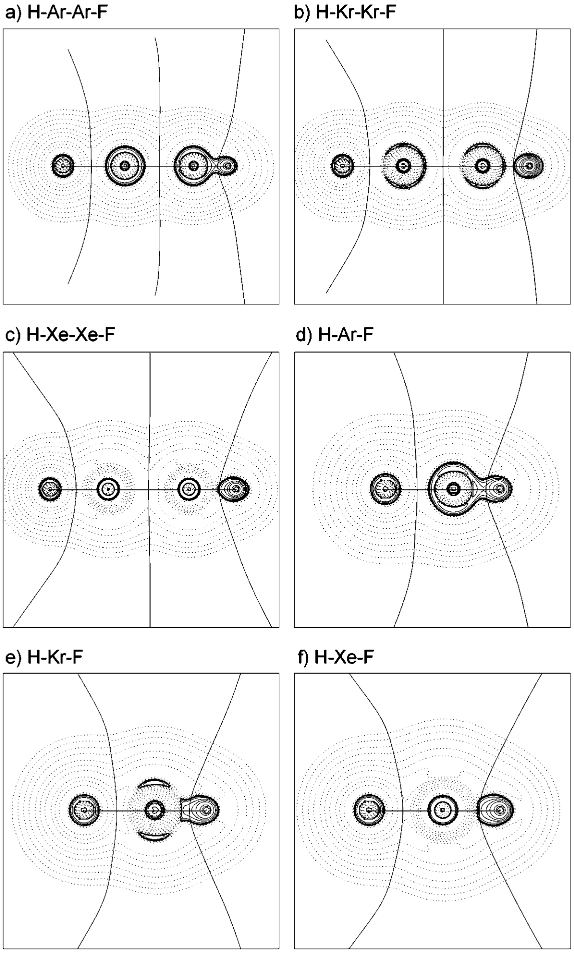

Figure 3. Contour line diagrams $\nabla^2\rho(r)$ of the calculated molecules. Solid lines indicate areas of charge concentration ($\nabla^2\rho(r) < 0$) while dashed lines show areas of charge depletion ($\nabla^2\rho(r) > 0$).

Table 3: AIM results of HNgNgF and HNgF at the MP2/def2-TZVPP//MP2/def2-TZVPP level.

Molecule	Bond	$\rho(r_b)$	$\nabla^2\rho(r_b)$	$H(r_b)$
H-Ar-Ar-F	H-Ar	0.229	−0.888	−0.274
	Ar-Ar	0.037	0.126	0.0002
	Ar-F	0.040	0.181	0.0014
H-Ar-F	H-Ar	0.293	−0.657	−0.229
	Ar-F	0.107	0.327	−0.028
H-Kr-Kr-F[a]	H-Kr	0.088	0.079	−0.039
	Kr-Kr	0.029	0.057	−0.0008
	Kr-F	0.056	0.151	−0.0035
H-Kr-F	H-Kr	0.192	−0.422	−0.165
	Kr-F	0.104	0.268	−0.034
H-Xe-Xe-F	H-Xe	0.111	−0.082	−0.063
	Xe-Xe	0.041	0.050	−0.0058
	Xe-F	0.079	0.204	−0.020
H-Xe-F	H-Xe	0.155	−0.196	−0.118
	Xe-F	0.098	0.225	−0.037

[a] Using the m05-2x/def2-TZVPP optimized geometry.

towards the hydrogen end than in the Ar—H fragments. The Kr—Kr bonding in HKrKrF exhibits a small polarization at the krypton atoms. The more polarizable xenon atoms in HXeXeF show an area of charge depletion $\nabla^2\rho(r) < 0$ (dashed lines) that agrees with the partial charges for the noble gas moiety Xe—Xe$^+$ (Table 2). Unlike the free Xe_2^+ cation, which was isolated by Seppelt, the compound HXeXeF has a covalent Xe—H bond in the HXeXe$^+$ fragment, which is bonded to F$^-$ mainly through Coulombic interactions.

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