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Prediction of a Metastable Helium Compound: HHeF

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Since the discovery of the first noble-gas compound by Bartlett in 1962,[1] the existence of compounds containing krypton, xenon, and radon was firmly established.[2,3] On the other hand, compounds of the lighter noble gases, namely helium, neon, and argon, remain nonexistence. The only serious candidate is ArBeO, observed in low-temperature matrices by Thompson and Andrews.[4] However, Frenking et al. indicated that the stability of this molecule is attributed solely to induced dipole interactions.[5,6] Helium, being the element with the highest ionization energy, is particularly difficult to form into a chemical bond. Although extensive theoretical and experimental studies have shown that helium is capable of forming stable covalent species in cations,[7,8] the existence of a neutral compound containing a helium chemical bond remains an illusive dream. Recently, a new class of xenon- and krypton-containing charge-transfer molecules, HX^+Y^- (X = Kr or Xe; Y = fragment with a large electron affinity), have been characterized by Pettersson, Räsänen, and co-workers.[9−13] Their elegant work has extended the known class of noble-gas bonds to Xe−H, Xe−I, Xe−Br, Xe−S, Xe−O, Kr−H, Kr−C, and Kr−Cl. It is intriguing to ask whether a similar type of charge-transfer molecule containing He, Ne, or Ar could exist? In this communication, the prediction of a metastable neutral helium compound is reported.

Ab initio calculations were carried out for a series of HNgF (Ng = He, Ne, Ar, and Kr) compounds. Geometries were fully optimized with the cc-pVTZ basis set at the B3-LYP and CCSD levels. Improved relative energies were obtained from CCSD(T) calculations with a larger cc-pVQZ basis set based on the CCSD optimized geometry. For the Kr atom, the cc-pVTZ and cc-pVQZ basis sets refer to the 6-311G(2df) and 6-311+G(3df) basis sets, respectively. To shed light on the bonding and charge distribution of these molecules, charge density analysis was performed using the Bader's theory of atoms in molecules (AIM)[14] and the natural bond orbital (NBO) approach.[15]

Optimized structural parameters are given in Table 1. As expected, the HNgF species have a linear equilibrium geometry and have a $^1\Sigma^+$ electronic ground state. These molecules have a somewhat long Ng−F bond. The Ng−H bond length in HNgF is slightly longer (by ~0.05 Å) than that in the corresponding NgH^+ cation. All HNgF species are characterized by a large degree of charge separation (dipole moment > 4.5 D), which is a characteristic of a charge-transfer species. Although HNeF is a bound species at the B3-LYP/cc-pVTZ level, it is calculated not to be stable at higher levels of theory. Surprisingly, HHeF is a bound species at all levels of theory.

Calculated dissociation energetics for the HNgF species are summarized in Table 2. Heterolytic dissociation to NgH^+ and F^- is a strongly endothermic process. Thus, the stabilization energies of these systems could be discussed in terms of the strong Coulomb attraction between the NgH^+ and F^- ion pair. The H + Ng + F dissociation limit is strongly dependent on the nature of the noble gas: exothermic for He and Ne, near thermoneutral for Ar and endothermic for Kr (Table 2). On the other hand, fragmentation to HF + Ng is predicted to be a strongly exothermic process for all species. It is worth noting that HF and Ng forms a van der Waals complex and this HF···Ng species is a prototypical system in the study of intermolecular forces.[16−18]

The stability of the HNgF species depends on the activation barrier for the lowest-energy fragmentation reaction (HNgF → HF + Ng). The transition state for this dissociation process is a bent structure (∠HNgH = 157, 104, and 101°, for He, Ar, and Kr, respectively).[19] Both HKrF and HArF are predicted to have a sufficiently large energy barrier (145 and 117 kJ mol^{-1}, respectively) that they could be observable in the gas phase. Indeed, HKrCl, which is calculated to have a similar stability (barrier height = 129 kJ mol^{-1}), has been observed by Pettersson et al. recently.[11] Remarkably, HHeF is predicted to exist with a significant potential energy well of 36 kJ mol^{-1}. It is important to note that these HNgF charge-transfer species may be strongly stabilized in a polar matrix environment. For instance, HHeF is calculated to have a stabilization energy of 40 kJ mol^{-1} (B3-LYP/cc-pVTZ) in a dielectric medium of $\epsilon = 40$, using the SCIPCM polarizable continuum model.[20] To facilitate future characterization of these species, the complete set of calculated harmonic vibrational frequencies (CCSD/cc-pVTZ) is given in Table 1.

To establish definitively the stability of HHeF, higher-level geometry optimizations were performed at CCSD/aug-cc-pVTZ and CCSD(T)/aug-cc-pVTZ levels. The augmented version of the cc-pVTZ basis set reduces the activation barrier significantly by 10 kJ mol^{-1}. On the other hand, inclusion of triple excitations increases the barrier height by 5 kJ mol^{-1}. At our best level of theory, CCSD(T)/aug-cc-pVQZ, HHeF is predicted to lie in a potential energy well of 33 kJ mol^{-1}.[21] Zero-point energy correction reduces the well depth by 5 kJ mol^{-1}. Hence, the existence of this intriguing helium-containing species is confirmed. However, this small potential energy well may pose a great challenge to the experimentalists for its detection.

What is the nature of bonding in this series of noble-gas compounds? Calculated AIM and NBO charge distributions and topological properties (Table 3) confirm the charge-transfer character of the HNgF compounds. In all cases, there is a large

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Table 1. Calculated Structural Parameters, Dipole Moments, and Harmonic Vibrational Frequencies[a]

	r(Ng−H) (Å)		*r*(Ng−F) (Å)			frequency[b] (cm^{-1})		
species	B3-LYP	CCSD	B3-LYP	CCSD	μ (D) B3-LYP	HNgF bend	Ng−F stretch	Ng−H stretch
HHeF	0.852	0.822	1.404	1.385	4.490	809	1037	2304
HNeF	1.278	*c*	1.957	*c*	5.504	*c*	*c*	*c*
HArF	1.386	1.334	1.986	1.967	5.776	767	488	2160
HKrF	1.514	1.468	2.037	2.019	5.145	733	463	2189

[a] cc-pVTZ basis set. [b] CCSD/cc-pVTZ level. [c] HNeF is not a stable species at the CCSD level.

Table 2. Calculated Relative Energeies (kJ mol^{-1})[a]

	transition state[b]			NgH$^+$ + F$^-$			Ng + H + F			HF + Ng		
Ng	B3-LYP	CCSD(T)	ZPE[c]	B3-LYP	CCSD(T)	ZPE[c]	B3-LYP	CCSD(T)	ZPE[c]	B3-LYP	CCSD(T)	ZPE[c]
He	48.9	36.4	−10.1	839.8	761.0	−11.7	−56.0	−90.1	-30.0	-629.8	-675.5	−5.6
Ne	19.9	*d*	*d*	689.9	*d*	*d*	−171.0	*d*	*d*	−744.8	*d*	*d*
Ar	150.9	117.2	−5.1	724.1	663.9	−8.5	25.9	10.4	−25.0	−547.9	−575.0	0.2
Kr	169.4	145.0	−4.6	756.7	694.9	−9.1	112.6	107.1	−24.6	−461.3	−478.3	0.6

[a] Relative to HNgF; B3-LYP/cc-pVTZ//B3-LYP/cc-pVTZ and CCSD(T)/cc-pVQZ//CCSD/cc-pVTZ levels. [b] Transition state for the HNgF → HF + Ng reaction. [c] Zero-point energy (ZPE) corrections were calculated at the CCSD/cc-pVTZ level. [d] HNeF is not a stable species at the CCSD level.

Table 3. Calculated Charge Distributions and Topological Properties at the Bond Critical Point[a]

	Ng−H		Ng−F		atomic charge[b]			
species	ρ_b	$\nabla^2\rho_b$	ρ_b	$\nabla^2\rho_b$	H	Ng	F	Ng in NgH$^+$
HHeF	0.245	−1.357	0.148	0.684	0.493 (0.307)	0.095 (0.332)	-0.588 (−0.639)	0.088 (0.266)
HNeF	0.105	0.146	0.045	0.369	0.355 (0.312)	0.042 (0.108)	-0.397 (−0.421)	0.099 (0.233)
HArF	0.217	−0.496	0.090	0.391	0.262 (0.179)	0.442 (0.562)	-0.704 (−0.741)	0.358 (0.534)
HKrF	0.186	−0.320	0.094	0.325	0.076 (0.075)	0.632 (0.672)	-0.708 (−0.747)	0.568 (0.628)

[a] Based on AIM analysis using the QCISD/6-311++G** wave function. [b] NBO charges (QCISD/6-311++G**) are given in parentheses.

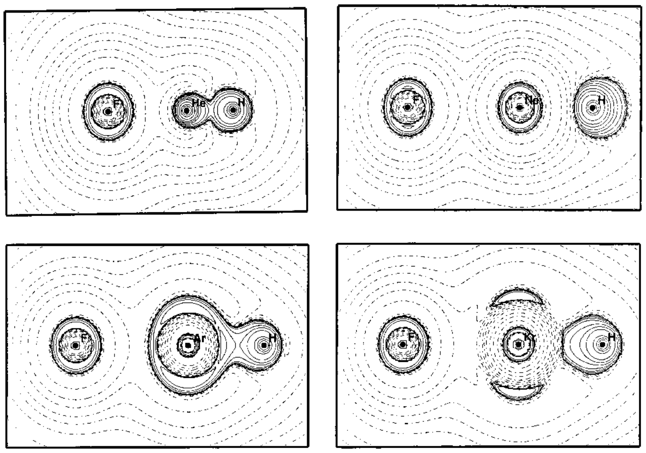

Figure 1. Contour line diagrams of the QCISD/6-311+G** Laplace concentrations $-\nabla^2\rho_b$ of (a) HHeF, (b) HNeF, (c) HArF, and (d) HKrF. Solid lines are in regions of charge concentration and dashed lines in regions of charge depletion.

degree of charge transfer from the F atom to the NgH moiety (ranging from 0.40 to 0.75 e). Interestingly, the amount of charge transfer increases in the order Ne < He < Ar < Kr. For HKrF and HArF, the positive charge locates mainly at the Ng atom. In sharp contrast, the Ne atom is only slightly polarized and the hydrogen atom carries a large positive charge for the neon analogue. For HHeF, NBO analysis leads to a significantly large positive charge at the He atom while the AIM value is somewhat smaller. The calculated positive Laplacian of electron density ($\nabla\rho_b$) at the Ng−F bond critical point (Table 3) indicates that the Ng−F bond is dominated by electrostatic attraction for all the HNgF species. On the other hand, the Ng−H bond is characterized by covalent interaction: $\nabla\rho_b < 0$ (except for HNeF). The Laplacian contour maps in Figure 1 clearly demonstrate the covalent and ionic contributions in HHeF, HArF, and HKrF. For HNeF, the electron density distributions of the H, Ne, and F atoms are hardly distorted.

As with multiply charged cations,[22] the ground-state reaction profile for the HNgF → HF + Ng fragmentation reaction can be satisfactorily described as arising from an avoided crossing between an attractive charge-transfer state (NgH^+-F^-) and a repulsive state corresponding to HF + Ng. Thus, a higher kinetic barrier may arise from a less repulsive state or a stronger NgH^+-F^- ion-pair interaction.

Since helium has a significantly higher ionization potential than neon, it is rather surprising that HHeF is more stable than HNeF. The unusual stability of HHeF may be understood in terms of its charge distribution. As pointed out earlier, strong positive charge lies at the hydrogen atom of HHeF and HNeF. Therefore, one would expect their stabilities to be dominated by the strong electrostatic interaction between the H and F atoms. The calculated H···F distance in HHeF (2.25 Å) is substantially shorter than that in HNeF (3.25 Å). Since Coulomb attraction energy is inversely proportional to the distance between charge centers, the NgH^+-F^- ion pair is significantly stronger in HHeF than in HNeF (by 135 kJ mol^{-1}, Table 2) and this attractive stabilization is sufficiently large that HHeF remains a bound species.[23]

In conclusion, the HNgF compounds are best described as charge-transfer species. The bonding of HHeF, HArF, and HKrF consists of covalent Ng−H and ionic Ng−F contributions. All HNgF species are calculated to be metastable with respect to HF + Ng. Remarkably, HHeF is also predicted to be a metastable species, which represents the first neutral compound containing a helium chemical bond. Although Frenking and co-workers have shown computationally that HeBeO is a bound species ($D_0 = 10$ kJ mol^{-1}),[6,23] the bonding in HeBeO was attributed to the strong charge-induced dipole interactions without covalent contribution.[6]

Supporting Information Available: Table of calculated structural parameters and energies of HHeF (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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