

Relativistic effects on the noble gas chemistry: A study of the HNgF → Ng + HF (Ng = Ar, Kr, Xe and Rn) decomposition reaction

Régis T. Santiago, Roberto L. A. Haiduke

Instituto de Química de São Carlos, Universidade de São Paulo, CP 780, 13560-970, São Carlos, SP, Brasil.

Actually, there is a growing interest in chemical reactions involving noble gases. The experimental evidence of molecules like HArF promoted a renewed interest on the noble gas research field [1-2]. However, some aspects are still unknown [2]. One of them is the importance of relativistic effects in reaction mechanism calculations by quantum chemistry methods. Decomposition pathways for HArF and HKrF were previously investigated by the Relativistic Effective Core Potential (RECP) method [3]. Thus, we performed a new study including Xe and Rn compounds along with more advanced relativistic treatments. Our objective is to analyze the relativistic effects for the decomposition pathway of HNgF (Ng = Ar, Kr, Xe and Rn) compounds into HF and a noble gas atom.

All the optimization, vibrational frequencies and Intrinsic Reaction Coordinate (IRC) calculations were done with the Gaussian 09 package [4]. We used the Density Functional Theory (B3LYP functional), aug-cc-pVTZ basis set for H, F, Ar and Kr and aug-cc-pVTZ-PP basis set for Xe and Rn atoms. The IRC calculations connected the reactants to the products of each investigated reaction. Next, the previously optimized structures were used in the DIRAC 16 program [5], by means of Coupled Cluster calculations with single and double iterative excitations along with perturbative triple substitutions (CCSD-T) and RPF-4Z basis sets [6]. Hence, we determined electronic energies in the non-relativistic (NR) and relativistic treatments, Dirac Coulomb (DC) and DC-SF (spin-free).

The electronic energies of activation (E_{act}) and energies changes (ΔE) for reactions with HArF and HKrF are in nice agreement with a previous study [2]. Table 1 shows our results (kcal mol⁻¹).

Table 1: Electronic energies of activation (E_{act}) and energies changes (ΔE) obtained with NR, DC-SF and DC treatments for each decomposition reaction (kcal mol⁻¹).

Reaction	Eact			ΔE		
	NR	DC-SF	DC	NR	DC-SF	DC
$HArF \rightarrow Ar + HF$	25.62	25.88	25.88	-135.32	-134.91	-134.91
$HKrF \rightarrow Kr + HF$	34.26	34.85	34.83	-115.64	-114.99	-114.91
$HXeF \rightarrow Xe + HF$	40.50	41.00	40.81	-91.19	-92.08	-91.70
$HRnF \rightarrow Rn + HF$	39.65	41.56	40.05	-80.31	-84.31	-80.96



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Firstly, analyzing the activation energies, we can notice that scalar relativistic effects increase E_{act} between 1.0 and 4.6%. On the other hand, spin orbit coupling corrections decrease this activation energy by as much as 3.8% (HRnF). Moreover, analyzing the energy differences between products and reactant, we can notice the same trend. Hence, there is a significant cancelation between scalar relativistic effects and spin-orbit coupling for compounds with the heaviest noble gases (Xe and Rn). Overall, the high barriers obtained indicate that all HNgF compounds are kinetically stable.

In summary, we conclude that relativistic effects can change significantly the energetics (E_{act} and ΔE) of these decomposition reactions. As expected, the HRnF compound showed the highest relativistic correction. Moreover, this investigation reveals a surprising cancellation between scalar relativistic affects and spin orbit coupling terms.

Key-words: relativistic effects, decomposition reaction, noble gas chemistry

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