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Bonding in radon hexafluoride: An unusual relativistic problem?

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Radon hexafluoride is a bound species (bond length Rn–F: 2.008 Å) as demonstrated by correlation corrected relativistic *ab initio* calculations using IORAmm (infinite order regular approximation with modified metric) at the MP2 level of theory with a (24s20p13d8f)[15s13p8d4f]/aug-cc-pVDZ basis set. The calculated atomization energy is 226.9 kcal mol^{-1} and the dissociation energy leading to Rn and $3F_2$ is 126.6 kcal mol^{-1}. Results are in line with simple orbital-based predictions of possible relativistic effects. The relativistic effect for the atomization energy is -10.8 kcal mol^{-1} rather than $+27.7$ kcal mol^{-1} as predicted on the basis of Dirac–Hartree–Fock (DHF) calculations. The latter were flawed by the lack of correlation corrections and an erroneous polynomial fit of the potential energy surface in the vicinity of the global minimum.

1. Introduction

Noble gas compounds have attracted the interest of chemists ever since Bartlett[1] made the discovery of the first noble gas compound.[2] While subsequent work tried to establish the chemistry of krypton and xenon,[2] later investigations driven in particular by the quantum chemical calculations of Frenking and Cremer[3] focused on the chemistry of neon and helium. However, little has been done with regard to the chemistry of radon (atomic number 86), probably because extensive experimental studies are confronted with the danger of radioactivity while quantum chemical calculations are complicated by the need of considering relativistic effects.

Recently, Malli[4] published all-electron Dirac–Hartree–Fock (DHF) calculations on octahedral RnF_6, which predict an enormous relativistic correction of *ca.* $+27.7$ kcal mol^{-1} for the atomization energy (AE) of RnF_6. The molecule is unbound both at the HF and at the DHF levels of theory, *i.e.* $AE < 0$. According to the calculated RnF bond length and AE value, the inclusion of relativistic effects leads to a strengthening of the RnF bond (shortening from 2.05 to 2.01 Å; improvement of AE from -104.7 kcal mol^{-1} to -77.0 kcal mol^{-1}).[4]

These results are in contradiction with effective core potential (ECP) calculations of Kaupp and co-workers[5] carried out at the MP2 level of theory. These authors[5] get for the binding energy of RnF_6 with respect to $Rn + 3F_2$ 137.0 kcal mol^{-1} at the non-relativistic ECP level and 117.4 kcal mol^{-1} at the relativistic ECP (RECP) level of theory suggesting that RnF_6 is bound and that the RnF bond becomes weaker rather than stronger due to relativistic effects.

In this work we describe results of an all-electron relativistic study, which was carried out to solve the contradiction between the DHF and RECP/MP2 description of RnF_6. Our results are based on the recently developed IORAmm/HF and IORAmm/MP2 (infinite order regular approximation with modified metric) methods[6,7] which have been shown to lead to reliable relativistically corrected descriptions. The IORAmm results will be rationalized with the help of simple orbital considerations and an explanation for the contradictory results of Malli[4] and Kaupp and co-workers[5] will be given.

2. Details of calculations

In the calculations on radon hexafluoride, the block-contracted [15s12p8d4f] and [15s13p8d4f] basis sets for radon were used. The basis sets were derived from the spin-free (24s20p13d8f) relativistic basis set of Dyall.[8] For the first basis set, the innermost three s-type and two p-type primitive functions and the outermost six s-type, five p-type, four d-type, and an f-type primitive functions were decontracted. The remaining fifteen s-type functions were block-contracted in a 4/3/2/2/2/2 pattern employing the contraction coefficients for 1s-, 2s-, 3s-, 4s-, 5s-, and 6s-orbitals. Thirteen p-type primitive functions remaining after decontraction were contracted in a 4/3/2/2/2 pattern using the contraction coefficients for 2p-, 3p-, 4p-, 5p-, and 6p-orbitals. Nine d-type primitives were block-contracted in a 4/3/2 pattern utilizing the coefficients for 3d-, 4d-, and 5d-orbitals. Seven f-type primitive functions were contracted to two orbitals using the coefficients of 4f-orbital in a pattern 4/3. The basis set obtained in this way was augmented with one d- and one f-type polarizing primitive function.[8] The [15s12p8d4f] basis set for radon obtained in this way was combined with the correlation consistent cc-pVDZ basis set of Dunning[9] for fluorine to give a [15s12p8d4f]/cc-pVDZ basis, henceforth called basis A.

A somewhat larger [15s13p8d4f] basis set on Rn is obtained from the previous basis set by decontracting the fifth contracted p-type basis function. Combination with the aug-cc-pVDZ basis set[9] for fluorine leads to a [15s13p8d4f]/aug-cc-pVDZ basis, henceforth called basis B. The use of an augmented basis set for fluorine is motivated by the high polarity of the Rn–F bond with the fluorine atom bearing an atomic charge close to -1 (see below). Note that the calculations reported in ref. 4 and earlier ECP calculations[10] of RnF_6 did not employ diffuse functions on F.

In the MP2 calculations of RnF_6, electrons 5s, 5p, 5d, 6s, and 6p of radon were correlated together with the 2s and 2p electrons of the fluorine atoms (68 electrons in total). The atomic calculations for fluorine were performed at spin-unrestricted level of theory. The molecular total energies calculated with IORAmm were corrected for the gauge shift error as described in refs. 6 and 7. Basis set superposition errors were corrected both in the relativistic and the non-relativistic

Table 1 Relativistic and non-relativistic properties of RnF_6 obtained at the HF level of theory

Parameter	IORAmm(A)[a]	NR(A)[a]	IORAmm(B)[b]	NR(B)[b]
r_e(Rn–F)/Å	1.968	1.989	1.953	1.971
E_{RnF_6}/E_h	−24 136.692101	−22 439.907280	−24 141.016466	−22 447.126376
E_{Rn}/E_h	−23 540.080037	−21 843.823798	−23 544.276429	−21 850.922623
E_F/E_h	−99.467187	−99.375328	−99.473866	−99.381806
r_e(F–F)/Å	1.343	1.343	1.337	1.337
E_{F_2}/E_h	−198.872117	−198.688533	−198.887862	−198.703999
AE(RnF_6)/kcal mol^{-1} [c]	−119.9	−105.6	−64.8	−54.7
ΔE_r/kcal mol^{-1} [d]	−2.7	11.2	48.0	57.6
$D_e(F_2)$/kcal mol^{-1} [e]	−39.1	−39.0	−37.6	−37.4

[a] Calculated with basis set A. [b] Calculated with basis set B. [c] Atomization energy. [d] Energy of the reaction $RnF_6 \rightarrow Rn + 3\ F_2$. [e] Dissociation energy of F_2. Experimental value 38.3 kcal mol^{-1}.[17]

calculations using the counterpoise method.[11] The molecular calculations on RnF_6 were carried out imposing an O_h symmetry constraint. The geometry was optimized pointwise using the Rn–F bond length as a variable. A single-point calculation was done at the optimized geometry. The natural bond orbital (NBO) analysis[12] was employed to determine reliable atomic charges. All calculations were performed with the help of the COLOGNE2002[13] suite of quantum chemical programs.

3. Results and discussion

In Table 1, the IORAmm/HF results are listed for basis A and basis B. They are qualitatively in agreement with the DHF results[4] in so far as RnF_6 is predicted to be unbound ($AE < 0$) at the lowest level of theory using basis A. Noteworthy is that an improvement of the basis from A to B leads to a stabilization of RnF_6 and stronger bonding as reflected by the calculated RnF bond lengths (relativistic: from 1.968 to 1.953 Å; non-relativistic: from 1.989 to 1.971 Å, see Table 1). Although these results are qualitatively in agreement with the DHF results[4] they differ in two ways from the latter: (a) The relativistic corrections weaken rather than strengthen the bond as can be seen by both the calculated AE and the energy of the reaction $RnF_6 \rightarrow Rn + 3F_2$.[14] (b) The relativistic correction to AE is just half as large (14.3; 10.1 kcal mol^{-1}, Table 1) as the DHF value (27.7 kcal mol^{-1} [4]) with a tendency to decrease in the case of basis set enlargement.

Use of a correlation corrected relativistic method such as IORAmm/MP2 leads to a drastic change in bonding (see Table 2). RnF_6 is now bound no matter whether basis A or B is employed. At the IORAmm/MP2/B level of theory an AE of 226.9 kcal mol^{-1} (relativistic correction: −10.8 kcal mol^{-1}, Table 2) is calculated. The corresponding energy for the reaction $RnF_6 \rightarrow Rn + 3F_2$ is 126.6 kcal mol^{-1} in reasonable agreement with the RECP/MP2 value of 117.4 kcal mol^{-1}.[5] Note, however, that only 6s and 6p electrons of Rn were correlated in ref. 5 at the MP2 level.

Correlation corrections included at the MP2 level of theory lead to a lengthening of the RnF bond (relativistic: from 1.953 to 2.008 Å; non-relativistic: from 1.971 to 2.022 Å) as is also observed for the F–F bond length (Tables 1 and 2). A similar correlation effect on the RnF bond length was found by Kaupp and co-workers[5] when using ECP (from 1.981 to 2.033 Å; RECP: from 1.963 to 2.017 Å). The relativistic effect on the RnF bond length is opposite to the correlation effect causing a weak decrease by 0.017 and 0.015 Å (Table 2), respectively.

Although the RnF bond becomes weaker by relativistic corrections (basis A: −5.8 kcal mol^{-1}; basis B: −10.8 kcal mol^{-1}, Table 2), the bond length decreases, which is contrary to common chemical understanding that a weaker bond should possess a longer bond length. This however is typical of relativistic effects. Relativity stabilizes the 6p-orbitals of Rn slightly (from −0.4251 (non-relativistic) to −0.4260 E_h (relativistic)) and the 6s-orbital strongly (from −0.8720 (non-relativistic) to −1.0688 E_h (relativistic)). This leads to a reduction of the covalent radius of radon and in consequence to a shorter RnF bond length. The bonding in RnF_6 is strongly polar in view of Pauling electronegativities of $\chi_{Rn} = 1.98$ and $\chi_F = 3.98$.[15] This is confirmed by the NBO atomic charges[12] calculated at the HF level with basis set A (relativistic: $q_{Rn} = +4.9644$, $q_F = -0.8274$; non-relativistic: $q_{Rn} = +5.0166$, $q_F = -0.8361$). Clearly, relativistic corrections lead to a small reduction of the atomic charges caused by a change in the orbital energies. This implies a reduction of the polar character of the Rn–F bonds and their weakening whereas one has to consider that the more polar a bond is, the stronger it becomes.

Clearly, RnF_6 is a bound molecule as one would also expect in view of its stable homologue XeF_6.[2] A correlation-corrected

Table 2 Relativistic and non-relativistic properties of RnF_6 obtained at the MP2 level of theory

Parameter	IORAmm(A)[a]	NR(A)[a]	IORAmm(B)[b]	NR(B)[b]
r_e(R–F)/Å	2.017	2.034	2.008	2.022
E_{RnF_6}/E_h	−24 138.757993	−22 441.920612	−24 143.220702	−22 449.293588
E_{Rn}/E_h	−23 540.8754702	−21 844.580403	−23 545.071028	−21 851.678966
E_F/E_h	−99.609979	−99.518070	−99.631314	−99.539293
r_e(F–F)/Å	1.419	1.419	1.425	1.425
E_{F_2}/E_h	−199.264603	−199.080753	−199.315947	−199.131876
AE(RnF_6)/kcal mol^{-1} [c]	139.7	145.5	226.9	237.7
ΔE_r/kcal mol^{-1} [d]	55.7	61.5	126.6	137.4
$D_e(F_2)$/kcal mol^{-1} [e]	28.0	28.0	33.5	33.4

[a] Calculated with basis set A. [b] Calculated with basis set B. [c] Atomization energy. [d] Energy of the reaction $RnF_6 \rightarrow Rn + 3F_2$. [e] Dissociation energy of F_2. Experimental value 38.3 kcal mol^{-1}.[17]

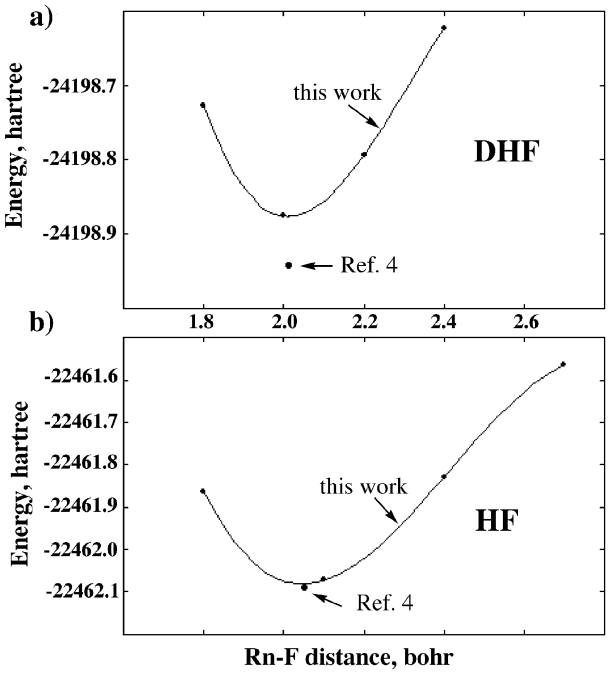

Fig. 1 The RnF_6 total energy from DHF (a) and non-relativistic HF (b) calculations reported in ref. 4 as a function of Rn–F distance. Small dots show the energies reported in Table 1 of ref. 4. Large dots show the interpolated energies reported in Table 2 of ref. 4. Solid lines show the curves obtained in this work by a polynomial interpolation performed with MATHEMATICA.

relativistic treatment of RnF_6 is absolutely necessary to give a reasonable account of its bond properties and in so far it is not astonishing that the DHF description of ref. 4 leads to an unbound molecule. It remains to be clarified why the DHF description predicts an unreasonably large relativistic correction of +27.7 kcal mol^{-1} for the AE[4] while the more reliable IORAmm/MP2 calculations predict just −10.8 kcal mol^{-1} (Table 2).

The spin–orbit interaction has little effect on the AE,[10] because RnF_6 and Rn are closed-shell species and F is a light element, and it cannot explain such a huge difference. In fact, as closer inspection reveals, the results of ref. 4 are based on a flawed geometry optimization procedure. The geometry was optimized numerically by constructing the potential energy curve from a polynomial interpolation on a one-dimensional grid of points in the vicinity of the global minimum of the potential energy surface (PES). Then, the total energy of a minimum of PES was obtained from the interpolated curve rather than carrying out a single point calculation of RnF_6 at the optimized geometry.[4] Fig. 1 shows in graphic form the results of DHF and non-relativistic HF calculations reported in ref. 4. As is obvious from Fig. 1, the interpolation procedure used in ref. 4 was corrupted because a polynomial interpolation with the MATHEMATICA package[16] using the data from Table 1 of ref. 4 (shown with small dots) does not reproduce the interpolated energy reported in ref. 4 (shown with large dots). For instance, the interpolated DHF energy for RnF_6 is −24 198.9418 E_h according to ref. 4, whereas the interpolation using the MATHEMATICA package yields −24 198.8760 E_h. For non-relativistic HF, the energies are −22 462.0897[4] and −22 462.0806 E_h (MATHEMATICA). The AEs reported in ref. 4 are −77.0 kcal mol^{-1} (DHF) and −104.7 kcal mol^{-1} (HF) while an interpolation with MATHEMATICA yields −118.3 kcal mol^{-1} (DHF) and −110.5 kcal mol^{-1} (HF). Hence, the corrected DHF energies of ref. 4 also indicate RnF bond weakening upon inclusion of relativistic effects, which is in line with our IORAmm results and resolves the contradiction between the ECP[5] and the DHF[4] descriptions of RnF_6.

4. Conclusions

Radon hexafluoride is a bound species as demonstrated by relativistically and correlation corrected *ab initio* calculations (IORAmm/MP2/B). The calculated AE is 226.9 kcal mol^{-1} and the binding energy with respect to Rn and $3F_2$ is 126.6 kcal mol^{-1}. The RnF bond length is predicted to be 2.008 Å. Our results are in line with a recent RECP/MP2 investigation which predicted 2.017 Å for the RnF bond length and 117.4 kcal mol^{-1} for the energy of dissociation in $Rn + 3F_2$.[5] They are also in agreement with simple orbital-based predictions of possible relativistic effects. The relativistic effect for the AE is −11 kcal mol^{-1} rather than +28 kcal mol^{-1} as predicted by Malli.[4] Malli's calculations[4] are flawed by the lack of correlation corrections and an erroneous polynomial fit of the PES in the vicinity of the global minimum. Hence, the inclusion of correlation effects is absolutely necessary to get a reliable relativistic description of RnF_6.

We note that octahedral RnF_6 may not represent the global minimum of the PES. Its homologue XeF_6 possesses in its crystal structure XeF_5^+ units with bridging fluoride anions inbetween so that two-thirds of the Xe atoms are seven-coordinate and one-third eight-coordinate.[18] Investigations are presently carried out in our laboratory to test the structural possibility also for RnF_6.

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