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The Heaviest Group 2 Difluoride, RaF_2: Geometry and Ionization Energy

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The heaviest group 2 difluoride, radium difluoride (RaF_2), is studied for the first time. A basis set is employed for radium that combines an effective core potential with a large, flexible valence space. This basis set is tested by calculating the first and second ionization energies of Ra, where values in excellent agreement with experiment are obtained. MP2 ab initio calculations are employed to obtain the optimized equilibrium geometry and the harmonic vibrational frequencies for the ground-state neutral and some of the low-lying cationic states. In addition, the optimized geometry of the ground-state neutral is obtained at the CCSD(T) level. The trend in geometry of the group 2 difluorides is confirmed, with a ∠FRaF bond angle of 118° being calculated, together with a bond length of 2.30 Å. It is concluded that involvement of the Ra 6p orbitals in the valence molecular orbitals of RaF_2 adequately explains its bent geometry. RCCSD(T) calculations are then employed to calculate ionization energies. The first adiabatic ionization energy, corresponding to the ionization $\tilde{X}^2\Sigma_u^+ \leftarrow \tilde{X}^1A_1$, is calculated to be 10.67 ± 0.05 eV. The ordering of the ionic states is discussed in the light of the present results. The polarizability of Ra was calculated to be 36.3 Å^3, with that of Ra^{2+} was calculated to be 1.97 Å^3; the latter was employed in a simple ionic model, but this failed to calculate the ionization energy accurately.

I. Introduction

The group 2 (group IIA) dihalides are an archetypal example of the breakdown of conclusions based on simple VSEPR theory[1] and Walsh diagrams.[2] They have been the subject of a wide range of studies over many years (see refs 3, 4 for thorough reviews), and it has been established that the equilibrium geometry of these molecules changes from linear to bent as the group is descended, for a particular halogen. This disagreement with the conclusions based on the original Walsh diagrams has been attributed to the noninclusion of d orbitals, and modified Walsh diagrams where d orbitals are included suggest bent structures;[5,6] however, polarization of the M^{2+} in an ionic picture may also be used to explain nonlinearity.[6−8] Hargittai has recently published a summary of the known theoretical and experimental information regarding these molecules,[4] which updates an earlier review.[3]

A number of years ago, we studied calcium difluoride,[9,10] which is the most difficult group 2 difluoride of which to predict the geometry, since it separates the linear BeF_2 (ref 9) and MgF_2 (refs 9 and 11) from the bent SrF_2 and BaF_2 (ref 12). Indeed there was a flurry of papers on CaF_2 in the early 1990s, which highlighted the need for a large, balanced flexible basis set. In particular, we note the work of Wright et al.[10] and Hassett and Marsden,[13] who studied the basis set requirements for this species in some depth. We also cite the earlier work of Klimenko et al.,[14] who noted that addition of d functions led to a bent equilibrium geometry, but that when 4p functions were added, a linear geometry was obtained, showing that balanced basis sets are required. The most recent study on CaF_2 appears to be that of Madden et al.[15] Very recently, to complete our study of the beryllium dihalides, BeX_2 ($X = F-I$[16]), we addressed the heaviest beryllium dihalide, $BeAt_2$,[17] as part of an initial study of diastatides. In the present work, we concentrate on the heaviest group 2 difluoride: RaF_2. Since the general trend for the group 2 dihalides is that as the metal gets heavier or the halide gets lighter, then the more bent the molecule becomes, then RaF_2 is expected to be the most bent group 2 dihalide.

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Nothing appears to be known about this molecule, probably owing to the radioactivity of radium.

II. Theoretical Details

The large number of electrons on Ra would make any all-electron calculation rather expensive, and so we elect to use effective core potentials (ECPs). We employed the relativistic CRENBL78 ECP.[18] As with our previous work employing ECPs,[17,19–24] we designed a large, flexible valence basis set, which contains a good description of the valence orbitals, as well as providing polarization, diffuse (and indeed diffuse polarization) functions. We tested the performance of the ECP for radium by calculating the first and second ionization energies of Ra: this was to ascertain that the basis set is flexible enough to describe both the neutral Ra atom and the Ra^{2+} cation. The group 2 dihalides are expected to have a large degree of ionic character, and so the ability to be able to describe $(Ra^{2+})\cdot 2(F^-)$ is important. The ionization of RaF_2 is expected to be largely located on the fluorine atoms, as has been noted in our previous work on BeX_2 (ref 16) and MgF_2 (ref 11), and consequently it is also important to be able to describe both F and F^-.

Radium has the electronic configuration $...5s^25p^65d^{10}4f^{14}6s^26p^67s^2$, and the orbitals up to and including the 4f are described by the ECP, with the 6s, 6p, and 7s being treated as valence, and are correlated in the MP2 and RCCSD(T) calculations (vide infra). All electrons on F except for the 1s shells are treated as valence and are included in the correlation treatments.

Three valence basis sets are designed, which all have one contracted s and one contracted p function, mainly describing the 6s and 6p electrons, respectively. These were obtained from a RHF calculation on Ra^{2+} employing a (17s17p) basis set, which was a set of even-tempered functions in both cases, with exponents ranging from 33.333333 to 0.0507479 (ratio = 1.5). The expansion coefficients from this RHF calculation were used to form the single contracted s and p functions. To the (17s17p)/[1s1p] set were added uncontracted functions, which are detailed below.

Basis Set 1
Ra Atom:
CRENBL78 ECP, plus [1s1p] from above, plus:
nine s,p: $\zeta = 5.0-0.0032768$, ratio = 2.5;
three d: $\zeta = 1.5, 0.375, 0.09375$, ratio = 4.0;
two f: $\zeta = 1.0, 0.2$, ratio = 5.0.
This may be designated CRENBL78[10s10p3d2f].
F atom:
6-311+G(3df).

Overall, this basis set has 147 basis functions and was used for geometry optimization and harmonic frequency calculations at the MP2 level.

Basis Set 2
Ra Atom:
CRENBL78 ECP, plus [1s1p] from above, plus:
nine s,p: $\zeta = 5.0-0.0032768$, ratio = 2.5;
four d: $\zeta = 2.5-0.0762939$, ratio = 3.2;
three f: $\zeta = 1.6, 0.4, 0.1$, ratio = 4.0.
This may be designated CRENBL78[10s10p4d3f].
F Atom:
aug-cc-pVTZ.

Overall, this basis set has 173 basis functions, and it was used for RCCSD(T) geometry optimization of the ground state of RaF_2.

Table 1. Calculated First and Double Ionization Energies of Radium

method	$Ra \rightarrow Ra^+ + e^-$	$Ra \rightarrow Ra^{2+} + 2e^-$
HF/basis set 3 (no *g*)[a]	4.350	13.864
MP2/basis set 3 (no *g*)[a]	5.195	15.318
HF/basis set 3[b]	4.369	13.864
RCCSD/basis set 3[b]	5.161	15.237
RCCSD(T)/basis set 3[b]	5.254	15.387
experimental[c]	5.279	15.421

[a] Projected (PUHF and PUMP2) total energies were used for the ^2S state of Ra^+; the basis set is the same as the CRENBL78[10s10p5d4f3g], but without the three g functions. [b] RHF and RCCSD(T) energies were used for all states. [c] From ref 27.

Basis Set 3
Ra Atom:
CRENBL78 ECP, plus [1s1p] from above, plus:
nine s,p: $\zeta = 5.0-0.0032768$, ratio = 2.5;
five d: $\zeta = 3.0-0.037037$, ratio = 3.0;
four f: $\zeta = 2.0-0.0610351$, ratio = 3.2;
three g: $\zeta = 1.6, 0.4, 0.1$, ratio = 4.0.
This basis set may be designated CRENBL78[10s10p5d4f3g].

F Atom:
aug-cc-pV5Z (no h functions).

Overall, this basis set has 330 basis functions and was used for single-point RCCSD(T) ionization energies of the ground state of RaF_2.

All (U)MP2 geometry optimizations and harmonic vibrational frequency calculations were performed using Gaussian98.[25] The (R)CCSD(T) calculations were carried out with MOLPRO2000.[26]

III. Results and Discussion

(a) Ionization Energies of Ra and Electron Affinity of F. The calculated ionization energies of radium at the different levels of theory are presented in Table 1. As may be seen, the agreement between experiment and the highest level of theory, RCCSD(T)/basis set 3, is excellent, with the first single ionization energy being calculated to within 0.025 eV of the

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Table 2. Optimized Geometrical Parameters, Computed Harmonic Vibrational Frequencies (cm^{-1}), Charge (q), and Spin Densities (ρ_s) of the Ground State of RaF_2 and Its Low-Lying Cationic States

							Ra		F	
state	energy/E_h	R_e/Å	θ_e/deg	$\omega_1(a_1)$ symm stretch	$\omega_2(a_1)$ bend	$\omega_3(b_2)$ asymm stretch	q	ρ_s	q	ρ_s
(U)MP2/Basis Set 1										
$\tilde{X}^1A_1$	−223.604898	2.3127	120.2	418.8	79.1	397.4	1.628	0.000	−0.814	0.000
saddle[a] $^1\Sigma_g^+$	−223.598474	2.3657	180.0	397.5	65.1i	368.8	1.641	0.000	−0.821	0.000
$^2B_2$[b]	−223.218192	2.2216	180.0	384.4	68.4	701.6	1.874	0.094	−0.437	0.453
$^2A_1$	−223.192725	2.2736	80.9	361.5	128.9	616.9	1.764	−0.003	−0.382	0.502
$^2A_2$[c]	−223.182165	2.4308	65.4	367.9	111.8	479.9	1.695	−0.099	−0.348	0.550
$^2B_1$	−223.183856	2.4351	93.5	348.7	55.2	483.0	1.714	−0.068	−0.357	0.534
CCSD(T)/Basis Set 2										
$\tilde{X}^1A_1$	−223.666016	2.2962	118.1							

[a] Optimized linear structure of the neutral (a saddle point), giving a barrier of linearity of 4.0 kcal/mol (1410 cm^{-1}); the vibrational frequencies have σ_g, π_u, and σ_u symmetries, respectively. [b] Became linear $^2\Sigma_u$ state; the vibrational frequencies have σ_g, π_u, and σ_u symmetries, respectively. [c] The computed F−F distance is 2.6254 Å.

experimental value of 5.279 eV[27] and the first double ionization energy being calculated to within 0.035 eV of the experimental value of 15.421 eV.[27] Thus, the basis set designed is performing very well for Ra, Ra^+, and Ra^{2+}, from which we infer that the radium will be well described no matter what charge it carries in RaF_2. For F^- we calculated the electron affinity at the RCCSD(T)/aug-cc-pV5Z (no h) level of theory, obtaining EA(F) = 3.3884 eV. The GIANT[28] and JANAF[29] tables cite EA(F) = 3.399 ± 0.003 eV, but the most precise value (cited by Lide[30]) seems to be that of Blondel et al.,[31] 3.401190 ± 0.000004 eV. The latter value corresponds to the process $F(^2P_{3/2}) + e^- \rightarrow F^-(^1S_0)$. The RCCSD(T) calculated value is an average of the electron affinities of the $^2P_{3/2}$ and the $^2P_{1/2}$ spin−orbit states; employing the experimental $^2P_{1/2}-{}^2P_{3/2}$ separation of 404 cm^{-1} (ref 27) allows an experimental average electron affinity of EA(F) = 3.389 eV to be calculated. Thus, the calculated RCCSD(T) value is in excellent agreement with the experimental one.

(b) Equilibrium Geometry of RaF_2. The optimized geometry of RaF_2 was obtained at the MP2/basis set 1 level of theory and is given in the first row of Table 2. Also obtained is the optimized geometry of the ground state constrained to a linear geometry (second row). The last row of Table 2 shows the optimized geometry at the CCSD(T) level of theory. Considering the first and last rows, it is clear that the optimized geometry of $RaF_2(\tilde{X}^1A_1)$ is fairly close to convergence, with the MP2/basis set 1 and CCSD(T)/basis set 2 results being in good agreement. We feel we can be confident in citing $\angle RaF_2 = 118°$ and $R_e = 2.30$ Å from these two results. The barrier to linearity at the MP2/basis set 1 level of theory could be derived as 1410 cm^{-1}, where no account of zero-point vibrational energy has been taken. This, together with the low bending frequency of 79 cm^{-1}, indicates a fairly shallow bending potential.

The bond angle of 118° is completely in line with the trend in bond angles, which have been determined approximately to be (based on the summary given in ref 4) 180° (BeF_2), 180° (MgF_2), 150−160° (CaF_2), 140−145° (SrF_2), and ∼125° (BaF_2). The results herein thus complete the set of geometrical parameters for the group 2 difluorides.

The calculated atomic charges (Table 2) suggest that RaF_2 is fairly ionic, with the Ra atom carrying a charge of $+1.6e$ and the fluorines each carrying a charge of $-0.8e$. These charges were obtained from Mulliken population analyses and so need to be treated with some caution, but should be qualitatively correct. Analysis of the molecular orbitals indicates that for some orbitals there are contributions from the Ra 6p atomic orbitals to the valence molecular orbitals, confirming that total ionicity is not present. The latter fact implies that caution should be employed when considering the results of calculations where the 6s and 6p orbitals are considered as "core": they clearly have some valence contribution, vide infra.

(c) Lowest Cationic States and Ionization Energies. The equilibrium geometries of the lowest cationic states of each symmetry are also presented in Table 2, obtained at the MP2/basis set 1 level of theory. The highest occupied molecular orbitals of RaF_2 in a linear orientation are calculated to be $...\sigma_g^2\pi_g^2\pi_u^2\sigma_u^2$ (in C_{2v} the ordering is thus expected to be $...a_1^2b_2^2a_2^2b_1^2a_1^2b_2^2$). In a completely ionic picture, one expects the π_g orbital (antibonding combination of F 2p) to be higher in energy than the π_u (bonding combination of F 2p); however, it is clear from the calculated SCF wave function that the Ra 6p orbitals are involved in the valence picture. The addition of the Ra 6p into the π_u orbital leads to an antibonding effect and, consequently, a destabilization of its energy; on the other hand, it is not possible, by symmetry, for the Ra 6p orbitals to contribute to the π_g orbital. Thus, the π_u orbital rises in energy relative to the π_g. Similarly, the Ra 6p orbital contributes to the σ_u orbital in an antibonding fashion, leading to an increase in its energy. These observations can in fact explain the nonlinearity of RaF_2, without recourse to the involvement of d orbitals nor the polarization of the core, vide infra.

For a linear molecule, four cationic states are expected upon ionization of the F 2p localized orbitals, but in C_{2v}, the number increases to six; if electron reorganization and electronic correlation is important, then the cationic state ordering will not necessarily be that expected from the molecular orbital ordering (vide infra). It is clear from the changes in both the calculated atomic charges, q, and spin densities, ρ_s, between the $\tilde{X}^1A_1$ state and those of the cations that the ionization of RaF_2 is localized on the F atoms, as expected, with RaF_2 being largely $F^-{-}Ra^{2+}{-}F^-$ and RaF_2^+ being largely $F^{-0.5}{-}Ra^{2+}{-}F^{-0.5}$, indicating that the electron is lost equally from the two fluorine atoms.

The lowest energy cationic state is calculated to be the $^2B_2$ state, which actually optimizes to a linear $^2\Sigma_u^+$ state. This result is completely in line with the conclusions of photoelectron work

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Table 3. Computed Adiabatic and Vertical Ionization Energies (eV) for the Low-Lying Cationic States of RaF_2[a]

	AIE			VIE		
states	MP2[b]	RCCSD[c]	RCCSD(T)[d]	MP2[b]	RCCSD[e]	RCCSD(T)[f]
$^2\Sigma_u/^2B_2$	10.52	10.79	10.67	10.98	11.26	11.15
$^2A_1$	11.22	11.40	11.28	11.48	12.36	12.19
$^2A_2$	11.46	11.60	11.51	11.85	12.16	12.01
$^2B_1$	11.50	11.75	11.63	11.68	11.94	11.79

[a] No correction for ZPVE has been made. [b] MP2/basis set 1. For the cations, the projected PUMP2 energies were employed; there was some spin contamination in the UMP2 wave functions, with $\langle S^2\rangle$ values of 0.80 (0.83), 0.81 (0.83), 0.83 (0.80), and 0.85 (0.78) in the AIE(VIE) calculations for the $^2B_2$, $^2A_1$, $^2B_1$, and $^2A_2$ states, respectively. [c] RCCSD/basis set 3//MP2/basis set 1. [d] RCCSD(T)/basis set 3//MP2/basis set 1. [e] RCCSD/basis set 3//RCCSD(T)/basis set 2. [f] RCCSD(T)/basis set 3//RCCSD(T)/basis set 2.

on the dichlorides,[32] which have shown that as the metal atom gets heavier, the $^2\Sigma_u^+$ state stabilizes in energy to become the ground cationic state; for the lighter dichlorides, the ground state is the $^2\Pi_g$ state. The explanation for this change in ordering has been discussed in ref 32 and has been attributed to the increasing ionicity as the group is descended. To our knowledge, the only photoelectron spectrum of a group 2 difluoride that has been reported is that of Dyke et al.[11] for MgF_2, where the $^2\Pi_g$ state was concluded to be the ground cationic state. In our recent study on the beryllium difluorides, we also concluded that the ground state of BeF_2^+ was $^2\Pi_g$, but that there was a significant Renner−Teller interaction, leading to a bent $\tilde{X}^2B_2$ state.

The next highest linear cationic states in energy for RaF_2^+ are expected to be $^2\Pi_u$ and the $^2\Pi_g$, which correlate to ($^2B_1$ and $^2A_1$) and ($^2B_2$ and $^2A_2$), respectively, in a nonlinear geometry; finally there should be a $^2\Sigma_g^+$($^2A_1$) state. Looking at the results in Table 3 and the computed wave function, it is clear that the lowest energy state is the $^2B_2$($^2\Sigma_u^+$) state. Analysis of the other cationic wave functions, together with a CIS/basis set 1//MP2/basis set 1(neutral) calculation, shows that upon bending, the b_2 component of the π_g orbital is destabilized in energy and the a_1 component of the π_u orbital is stabilized. There are two states not included in Table 2: the $^2B_2$ state arising from single occupancy of the b_2 component of the π_g orbital; the $^1A_1$ state arising from single occupancy of the σ_g (a_1) orbital. These states are more difficult to study, as SCF methods tend to converge to the lowest state of a particular symmetry; they could be studied by MRCI methods, but that is beyond the scope of the present study.

In Table 3 are presented the calculated ionization energies of the lowest states of each symmetry at the MP2, RCCSD, and RCCSD(T) level of theory; both the adiabatic and vertical ionization energies were calculated from single-point energy calculations, with the geometries employed noted in the footnotes to this table. In Table 4 are shown the calculated energy separations between the states, including those from the CIS calculation (which allows all of the relevant states to be obtained). Looking first at Table 3, it may be seen that the calculated adiabatic ionization energies (AIEs) indicate the same ordering at the MP2, RCCSD, and RCCSD(T) levels of theory; consequently, the ordering of these four cationic states seems to be firmly established. For the vertical ionization energies (VIEs), the ordering changes from MP2 to RCCSD; the ordering at the RCCSD and RCCSD(T) is, however, the same, suggesting that this ordering is reliable. The energy gap between the AIE and the VIE gives an indication of the width expected for an observed photoelectron band, and it is clear that these will range from 0.2 to 0.9 eV, with the $^2A_1$ state expected to give rise to a very broad feature. The changes in the bond angle from the neutral state to the cationic states (see Table 2) suggest that the main structure will be a progression in the bending vibration; however, contributions from the symmetric stretch may contribute as well, to a small extent. Note that a second $^2A_1$ state is expected higher in energy and that there will be a second $^2B_2$ state within the 10.6−12.2 eV range. This latter fact is illustrated by the relative energies calculated at the CIS level (Table 4). The CIS method gives an estimate of the energy of all states accessible by a single-electron excitation from the ground cationic state and shows the approximate position of the $^2B_2$ and $^2A_1$ states, not obtained in the other calculations. It is clear by comparison with the higher level results, however, that the CIS method does not perform very well, as far as absolute energy is concerned. Table 4 also includes the Koopmans' theorem results, and it is immediately clear that electron correlation and probably orbital relaxation are affecting the cationic state energy orderings by comparing with the results of the MP2, RCCSD, and RCCSD(T) results. It is clear that the RCCSD method is required for reliable results and that only minimal change occurs when triple excitations are included.

Table 4. Relative Energies ($\Delta T_{\mathrm{Vertical}}$ and $\Delta T_{\mathrm{Adiabatic}}$)/eV of Low-Lying Cationic States of RaF_2^+ at Different Levels of Calculations[a]

states	$\Delta T_{\mathrm{vertical}}$ [$\Delta T_{\mathrm{adiabatic}}$]				
(linear MO)	KT[b]	CIS[c]	MP2[d]	RCCSD[e]	RCCSD(T)[f]
$^2B_2$ (σ_u)	0.0	0.0	0.0	0.0	0.0
$^2A_1$ (π_u)	0.60	1.23	0.96 [0.70]	1.57 [0.61]	1.52 [0.61]
$^2A_2$ (π_g)	1.09	2.31	1.33 [0.94]	1.37 [0.81]	1.34 [0.84]
$^2B_2$ (π_g)	1.13	1.66			
$^2B_1$ (π_u)	0.86	2.13	1.16 [0.98]	1.15 [0.96]	1.12 [0.96]
$^2A_1$ (σ_g)	1.37	2.56			

[a] Energies given relative to the respective ground-state cationic energy. [b] Koopmans' theorem results. Molecular orbital energies obtained from an SCF calculation at the neutral RCCSD(T)/basis set 2 optimized geometry. [c] CIS/basis set 1//MP2/basis set 1. [d] MP2/basis set 1 [e] RCCSD/basis set 3//RCCSD(T)/basis set 2 for T_{vertical}; RCCSD/basis set 3//MP2/basis set 1 for $T_{\mathrm{adiabatic}}$. [f] RCCSD(T)/basis set 3//RCCSD(T)/basis set 2 for T_{vertical}; RCCSD(T)/basis set 3//MP2/basis set 1 for $T_{\mathrm{adiabatic}}$.

(d) Ionic Model. It is also of interest to calculate the ionization energy of RaF_2 in the ionic model. The ionic model was originally devised by Rittner[33] and has been used by Lee and Potts[32] and Dyke et al.[11] to calculate classical ionization energies, with the results being in reasonably close agreement with experiment. The relevant equation is

$$\mathrm{IE(RaF_2)} = \mathrm{EA(F)} + \left(\frac{2.88}{r_e} - \frac{0.72}{r_e \cos\gamma}\right) + \frac{7.2 \times 10^{-4}}{r_e^{\,4}}(\alpha_{\mathrm{Ra^{2+}}} + \alpha_{\mathrm{F^-}} - \alpha_{\mathrm{F}}) \quad (1)$$

where γ is 1/2(180° − ∠FRaF), and the α_i are the relevant static polarizabilities. We employ values of EA(F) = 3.401190 eV (ref 31), r_e = 0.22962 nm, and ∠FRaF = 118° [RCCSD(T)/basis set 2 result, this work], $\alpha_{\mathrm{F^-}}$ = 0.64 Å^3 (from ref 34 but we note that early values close to 1 Å^3 have been reported[35]), and α_{F} = 0.557 Å^3 (ref 30). The polarizability of Ra^{2+} has not

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(32) Lee, E. P. F.; Potts, A. W. *Proc. R. Soc. A* **1979**, *365*, 395.

(33) Rittner, E. S. *J. Chem. Phys.* **1951**, *19*, 1030.

(34) Tessman, J. R.; Khan, A. H. *Phys. Rev.* **1953**, *92*, 890.

(35) See, for example, Pauling, L. *Proc. R. Soc. A* **1927**, *114*, 191.

been reported, to our knowledge, and so we initially estimated a value of $\alpha_{Ra^{2+}} = 2$ Å^3 from the trend in the group 2 neutral atom polarizabilities[30] and the polarizabilities of the other group 2 metal dications;[34] subsequently, we calculated this quantity at the CCSD(T)/basis set 3 level of theory, obtaining a value of 1.97 Å^3. To verify the accuracy of this number, we also calculated the polarizability of the neutral Ra atom at the same level of theory, obtaining a value of 36.3 Å^3, which may be compared to the available value of 38.3 Å^3 (ref 36). Using these values for the parameters in eq 1 allows IE(RaF_2) to be calculated as 12.81 eV. This value should be compared to some average of the vertical ionizations in the last column of Table 3, since all of these ionizations are the removal of an electron from a fluorine atom; this suggests that the calculated ionic model is ca. 1 eV higher than the values presented in Table 3. This is not totally unexpected, since first, some parameters employed are estimates and second it is demonstrated from the calculated atomic charges in Table 2 that RaF_2 is not completely ionic, and hence the Rittner model is expected to overestimate the IE, as observed. In addition, if RaF_2 were completely ionic, then it would be expected to be linear, which it clearly is not.

(e) The Nonlinearity of RaF_2. The most significant (although not entirely unexpected) result from the present study is that RaF_2 is calculated to be bent, even though the ECP employed does not allow for the core (below the 6s orbital) to polarize (since there are no coefficients to vary). The question must therefore be asked, what makes RaF_2 bent? The obvious answer would be the involvement of atomic d functions, which will effectively model the 6d orbitals; however, inspection of the wave function suggests that such an involvement is very small. The largest involvement is the Ra 6p atomic orbitals, as noted above. In fact, a consideration of the composition of the molecular orbitals as RaF_2 goes from linear to bent can explain why the bent geometry is lower in energy. The HOMO in RaF_2 is a σ_u orbital formed mainly by an antibonding combination of the F 2p in-plane orbitals, lying at a calculated energy of -12.1 eV. An Ra 6p orbital can also interact with this orbital in an antibonding fashion, leading to its rising in energy. If the molecule bends, then the overlap between the Ra and F orbitals is reduced, and the molecule is more stable. Similarly, the π_u orbital calculated to lie at -13.3 eV, formed mainly by a bonding combination of F 2p orbitals, is destabilized by the involvement of Ra 6p orbitals in an antibonding fashion when RaF_2 is linear, but that upon bending, this involvement is reduced, and hence the molecule is stabilized. No interaction between the π_g (calculated to lie at -13.5 eV) nor the σ_g (calculated to lie at -14.2 eV) linear combinations of F 2p orbitals and the Ra 6p orbitals is possible by symmetry. Consequently, the geometry of RaF_2 is adequately explained by a competition between ionicity (which would lead to a linear geometry) and some covalent antibonding character being introduced by the interaction of the Ra 6p and the F 2p orbitals in the linear orientation, which causes the molecule to bend to minimize this. In some ways, this involvement of the Ra 6p orbitals may be thought of as "polarizing the core", with the Ra atom's electron density being distorted along the intermolecular axis in a linear orientation; however, the form of the wave function, to us, suggests that a better picture may simply be that the 6p orbitals are acting as valence. The trend identified in previous work, and summarized in refs 3 and 4, that as the metal atom gets heavier, the tendency is more toward bent geometries, can be explained by the observation that the heavier M becomes, the closer in energy the $(n-1)$p and ns orbitals become, and so the more valence the $(n-1)$p orbitals become, and hence the more the molecule will bend as it attempts to minimize the destabilizing interaction of the $(n-1)$p orbitals.

Since radium is very close in the periodic table to the actinides, it is instructive (as pointed out by the referees) to compare the results herein with, for example, the equilibrium geometry of the isoelectronic UO_2^{2+} and ThO_2. In the case of UO_2^{2+}, the equilibrium geometry is established as bent, whereas that of ThO_2 is linear.[37] Theoretical studies have, however, differed in their explanation as to why this is so, with two pertinent recent studies being those of Dyall[38] and Kaltsoyannis.[39] Essentially two main mechanisms are under debate, which involve the destabilization of the σ_u HOMO. One explanation is that this is due to poor U/Th f_σ/O p_σ overlap, and the other is due to "pushing from below", where the U/Th 6p orbital interacts with the σ_u HOMO, destabilizing it. The conclusion of the most recent paper[39] on UO_2^{2+} is that it is the latter effect that is the most important. Evidence for this was provided by considering the orbital energies and compositions when the 6p orbitals were in-core or valence. Moving the 6p orbitals into the valence region significantly destabilized the σ_u HOMO, but the composition changed very little, with a small reduction in the O 2p contribution (-7%) and a small addition (8%) of U 6p character. Note that the latter conclusions are largely contrary to those reached by Dyall.[38]

Comparing to the present case, we first of all note that the 6p orbital is always included in the valence region herein. Since only one ECP was available to us, we were unable to vary the valence/core regions of the calculations. In some ways, the conclusions we reach are similar to those for UO_2^{2+} in that the 6p orbital destabilizes the σ_u orbital significantly; however, the contribution of the 6p orbitals to the σ_u HOMO is much greater in the present case, being 40%. Thus, we are not so sure that we would describe the destablization of the RaF_2 σ_u orbital as a "pushing from below", but more as a further antibonding contribution of the 6p to the mainly F 2p antibonding orbital; we emphasize that the wave function is very clear on this point. Upon bending, the σ_u orbital stabilizes by ca. 0.5 eV. The π_u orbital again has a definite contribution from the Ra 6p orbital, but in this case the contribution is only ca. 4%; the π_u orbital splits upon bending into a_1 and b_1 orbitals, with the a_1 component remaining unchanged in energy, whereas the b_1 component is stabilized by ~0.2 eV. Interestingly, the π_g orbital, which has almost no contribution from Ra orbitals (contributions from the Ra 6p orbital are symmetry forbidden), exhibits the same behavior as the π_u orbital, by splitting into an a_2 and a b_2 component, which remains almost unchanged in energy, being stabilized by ~0.2 eV. The σ_g orbital is destabilized upon bending, by ~0.2 eV. Thus the picture seems to be clear that upon bending, the π_u, π_g, and σ_g orbitals vary in energy by ca. 0.2 eV, but the largest difference is the energy of the σ_u orbital, which stabilizes by 0.5 eV.

IV. Conclusions

High-level ab initio calculations have been presented on the heaviest group 2 difluoride, RaF_2. In line with expectations, it is the most bent of the series, with a bond angle of 118°. RaF_2 is deduced to be fairly ionic from calculated atomic charges, but far from completely so. The calculated wave function suggests that the Ra 6p orbitals are involved in the bonding to

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(36) Doolen, G. D. Los Alamos Natl. Lab., unpublished, cited in ref 30.

(37) Pepper, M.; Bursten, B. E. *Chem. Rev.* **1991**, *91*, 719. Denning, R. G. *Struct. Bonding* **1992**, *79*, 215.

(38) Dyall, K. G. *Mol. Phys.* **1999**, *96*, 511.

(39) Kaltsoyannis, N. *Inorg. Chem.* **2000**, *39*, 6009.

a significant extent, and indeed a consideration of this involvement allows a rationalization of the bent structure of RaF_2. It is concluded that the involvement of d orbitals is minimal, but that the involvement of the 6p orbitals is significant.

The first adiabatic ionization energy is calculated to be 10.67 ± 0.05 eV, which corresponds to the ionization $\tilde{X}^2\Sigma_u^+ \leftarrow \tilde{X}^1A_1$. That the ground state is calculated to be a $^2\Sigma_u^+$ state is in line with previous conclusions from a series of photoelectron studies of the group 2 dihalides by Lee and Potts, where the $^2\Sigma_u^+$ state is stabilized in energy as the metal atom gets heavier. Calculations of the AIEs and VIEs for the lowest cationic state of each of the four C_{2v} group symmetry are reported, and the ordering of these states appears to be reliable.

The calculation of the ionization energy using an approximate Rittner ionic model led to a result that is significantly higher than the ionization energies calculated at the highest level of theory herein.

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