Structure and Bond Nature of the UF_5 Monomer

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The structure and bond nature for the ground state of the UF_5 monomer have been investigated by means of relativistic and nonrelativistic discrete-variational (DV) Xα molecular orbital (MO) methods. It is found that the nonrelativistic calculation provides only less than half of the U−F bond overlap population obtained by the relativistic calculation for the monomer with the C_{4v} geometry which was determined experimentally. Comparison of the U−F bond overlap population and valence level structures between the C_{4v} and D_{3h} geometries indicates that the stability of the D_{3h} monomer is almost equal to that of the C_{4v} one. Furthermore, it is confirmed that an intermediate structure (C_{2v}) between the two geometries shows similar values of effective charge, orbital, and bond overlap populations. This suggests that the energy barrier between the $D_{3\mathrm{h}}$ and C_{4v} geometries is very small and the geometry of the UF_5 monomer is fluxional between the C_{4v} and D_{3h} symmetries. This is consistent with the previous results reported by the Hartree−Fock method with relativistic effective core potentials [Wadt, W. R.; Hay, P. J. *J. Am. Chem. Soc.* **1979**, *101*, 5198]. The flexibility of the UF_5 structure originates from the fact that the U 5f atomic orbitals, which play a major role in the U−F bonding interactions, spread with wide angular distributions of the electrons in hybridization with the U 6d atomic orbital.

I. Introduction

The UF_5 monomer is a nascent product in the molecular laser isotope separation (MLIS) of uranium. Understanding its chemical properties is not only of importance for the development of the MLIS but also of interest in the relativistic effects on the chemical bonding of the monomer. Unfortunately, there have been only a few experimental[1−3] and theoretical[4,5] reports on the electronic structure and atomic configuration of the monomer to date.

The geometry of the UF_5 monomer, which was formed by the UV photolysis of UF_6 in an argon matrix, has been investigated by IR and Raman spectroscopy.[1−3] The equilibrium geometry of the monomer has been determined to be a square-pyramid of the C_{4v} symmetry with the U−F(axial) and U−F(equatorial) bond lengths of 2.00 and 2.02 Å, respectively, and with the F(axial)−U−F(equatorial) bond angle of 101°.

Rosén and Fricke[4] reported the Hartree−Fock-Slater and Dirac−Slater molecular orbital (MO) calculations for UF_5 with the experimentally determined structure of C_{4v} symmetry. They revealed the relativistic effects on the electronic structure but did not discuss the relativistic effects on the chemical bonding for the UF_5 monomer. On the other hand, Wadt and Hay[5] performed MO calculations for the geometry and electronic structure of the UF_5 monomer using the Hartree−Fock MO method with a relativistic effective core potential approximation. They showed that the monomer with C_{4v} geometry is slightly more stable, by about 1 kcal/mol (0.04 eV), than that with C_{4v} geometry in the presence of spin−orbit interaction. The distinct difference between the two structures is that the UF_5 monomer with C_{4v} geometry has a permanent dipole while that with D_{3h} geometry does not. According to their report, the stabilization energy due to the dipole interacting with the inert-gas matrix was estimated to be less than 0.2 kcal/mol which corresponds to a temperature of about 100 K. Since the above experiments have been carried out at less than 20 K, the C_{4v} geometry could not convert to the D_{3h} geometry but remained in the matrix. In gas phase at room temperature, it is possible for the UF_5 monomer to have another geometry such as D_{3h} rather than C_{4v} geometry. From the above reasons, Wadt and Hay have concluded that the structure of the UF_5 monomer is fluxional between the C_{4v} and D_{3h} geometries.

Why does the uranium atom have such a flexible bond against the change in geometry? They showed that both geometries have almost equal values of orbital population and total energy, but did not provide a qualitative interpretation on the origin of the fluxional structure of the UF_5 monomer.

The aim of the present work is to answer the above question. In order to discuss the flexible bond of the UF_5 monomer, we examined the relation between the geometry and bond nature of UF_5 using the bond overlap population. The bond overlap population and valence level structures of the monomer with the C_{4v} and D_{3h} geometries (see Figure 1) were investigated by the nonrelativistic discrete-variational Hartree−Fock-Slater (DV-HFS) and relativistic DV Dirac−Slater (DV-DS) methods. The bond overlap populations obtained by the Mulliken population analysis[6] are useful for understanding the characteristics of chemical bonding for different molecular structures qualitatively. In addition, since the DV-DS method directly provides the

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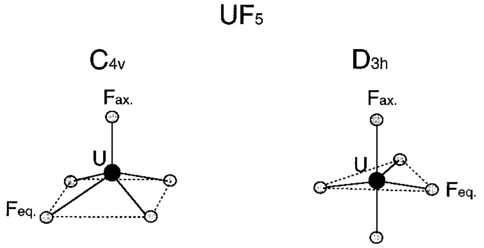

Figure 1. Schematic illustration of C_{4v} (U−F_{ax} = 2.00 Å, U−F_{eq} = 2.02 Å, F_{ax}−U−F_{eq} = 101°) and D_{3h} (U−F_{ax} = 2.00 Å, U−F_{eq} = 2.02 Å, F_{ax}−U−F_{eq} = 90°) geometries, which were experimentally and theoretically determined, respectively, for the UF_5 monomer.

relativistic effects in the framework of Slater's exchange potential approximation, this method is suitable for the study of the chemical bonding of molecules containing heavy atoms.[7−17]

In the present paper, computational procedures of the DV-HFS and DV-DS methods are briefly described in section II. We demonstrate in section III that the relativistic effects are very important for the chemical bonding of the molecules containing heavy elements such as uranium from the results of one-electron energies, orbital components, and bond overlap populations for the valence level structure of the UF_5 monomer with the C_{4v} geometry. In section IV, we compare the bonding stability between the C_{4v} and D_{3h} geometries on the basis of the results obtained using the Mulliken population analysis.

II. Computational Details

The one-electron Hamiltonian in the Dirac−Slater MO method is expressed as

$$H = c\alpha\mathbf{P} + \beta mc^2 + V(\mathbf{r}) \qquad (1)$$

where c, $\mathbf{P}$, m, α, β, and $V(\mathbf{r})$ denote the velocity of light, the momentum operator, the mass of an electron, the Dirac matrices, and the sum of the Coulomb and exchange potentials, respectively. The exchange potential used here was expressed in the same manner for nonrelativistic calculations, because relativistic corrections in the exchange potential are negligible in the valence region which is related to chemical bonding.[18] The computational details of the nonrelativistic and relativistic calculations have been described elsewhere.[19−22] It has been confirmed that electronic structures obtained with the nonrelativistic and relativistic Xα methods agree with each other for molecules containing light elements such as CF_4 and SF_6,[12,23] where the relativistic effects are negligible.

The molecular wave functions were expressed as linear combinations of atomic orbitals obtained by numerically solving the Dirac−Slater or Hartree−Fock−Slater equations in the atomic like potential derived from the spherical average of the molecular charge density around the nuclei. Thus the atomic orbitals which are employed as basis functions were automatically optimized for the molecule.[20]

Two-center charge densities are partitioned into one-center (atomic) charges by means of the Mulliken population analysis[6] in the self-consistent charge (SCC) method,[24] which was used to approximate the self-consistent field. According to the population analysis, the bond overlap population P_B(k,l) for the diatomic molecule consisting of k and l atoms is defined by

$$\mathbf{P_B}(\mathrm{k,l}) = \sum_i \sum_{r,s} 2N(i) C_{ir}^{\;\mathrm{k}} C_{is}^{\;\mathrm{l}} <\phi_r^{\;\mathrm{k}}|\phi_s^{\;\mathrm{l}}> \qquad (2)$$

In eq 1, i means the ith molecular orbital and $N(i)$ denotes the occupation number of electrons in the ith MO. The quantities C_{ir}^{k} and C_{is}^{l} represent the coefficients of normalized atomic orbitals ϕ_r^{k} and ϕ_s^{l} of the k and l atoms in the linear combination of these atomic orbitals for the ith MO, respectively. In the case of polyatomic molecules, $\mathbf{P_B}$ is given as a sum of all pairs of atoms by

$$\mathbf{P_B} = \sum_{\mathrm{k,l}} \mathbf{P_B}(\mathrm{k,l}) \qquad (3)$$

Since the Mulliken populations somewhat depend on the choice of basis sets, we used the same basis set (U, 1s−7p; F, 1s−2p) for both geometries of UF_5 monomer. Consequently, comparison of Mulliken populations of similar systems or a given molecule in the same basis set is valid and useful for understanding chemical properties.[25]

Molecular geometries of the UF_5 monomer were assumed to be C_{4v} and D_{3h} geometries with their bond lengths taken from experimental (U−F_{ax} = 2.00 Å, U−F_{eq} = 2.02 Å, F_{ax}-U-F_{eq}angle = 101°)[1] and theoretical (U−F_{ax} = 1.99 Å, U−F_{eq} = 2.02 Å, F_{ax}−U−F_{eq} angle = 90°)[5] results, respectively. The symbols F_{eq} and F_{ax} denote the equatorial and axial fluorine atoms in the C_{4v} and D_{3h} geometries as shown in Figure 1. As the spin function is included in eq 1, spin is coupled with spatial angular momenta, which leads to half-integral angular momenta. Although the normal point group symmetry satisfies the correlation of the electronic states obtained from integral angular momenta, this cannot be applied to the case of half-integral angular momentum states. In order to overcome this problem, Bethe introduced the idea of double group symmetry.[26] After that, Slater applied double groups to solve the Dirac−Slater Hamiltonian for the study of the relativistic effects in molecules and solids.[27] In the present study, the C_{4v} and D_{3h} point symmetry groups reduce to the C_{4v}* and D_{3h}* double groups in the DV-DS calculations, respectively. Symmetry orbitals corresponding to irreducible representations of these double group symmetries were constructed from the atomic orbitals using the projection operator method.[28] The DV-DS and DV-HFS calculations were performed using the Slater exchange parameter α of 0.7 for all the atoms and using 6000 DV sample points, which provided a precision of less than 0.1 eV for valence-electron energy eigenvalues. The charge distribution was taken to be self-consistent when the difference in orbital populations between the initial and final stages of the iteration became less than 0.01.

III. Relativistic Effects on Chemical Bonding of the UF_5 Monomer

In a recent paper,[12] we demonstrated that the relativistic effects are very important for understanding the chemical bonding in molecules containing elements with atomic numbers greater than 50. In order to confirm that the effects are marked

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Table 1. Bond Overlap Populations between Uranium and Fluorine Valence Orbitals Obtained Using the Nonrelativistic and Relativistic DV-Xα Calculations for UF_5 with C_{4v} Geometry

		bond overlap population	
		F_{eq}	F_{ax}
nonrel	U	+0.63	+0.11
rel	U	+1.43	+0.36

in 5f-electron systems, we examined the bond overlap populations ($\mathbf{P_B}$) of UF_5 (C_{4v}) using the nonrelativistic DV-HFS and relativistic DV-DS calculations, because $\mathbf{P_B}$ is a good indicator of the strength of covalent bonding. Table 1 shows the bond overlap populations between the uranium and fluorine atomic orbitals for the two calculations. It is found that the nonrelativistic calculation provides less than half of the bond overlap populations obtained by the relativistic calculation for both U−F_{eq} and U−F_{ax} interactions. This indicates that the relativistic calculation should be used in the study of the chemical bonding in actinide compounds.

In order to investigate the contribution of the U 5f atomic orbital to the U−F bond formation, the $\mathbf{P_B}$ values between the uranium and fluorine valence atomic orbitals were examined via the nonrelativistic and relativistic calculations. In the relativistic case, it is found that the U 5f−F 2s,2p interactions ($\mathbf{P_B}$ = 1.11) contribute significantly to the U−F bond as well as the U6d−F 2s,2p ones ($\mathbf{P_B}$ = 1.66). On the other hand, the nonrelativistic calculation shows that the U6d−F 2s,2p interactions ($\mathbf{P_B}$ = 1.49) mainly contribute to the U−F bond formation, while the U 5f atomic orbital plays a minor role ($\mathbf{P_B}$ = 0.35). This means that the U 5f−F 2s,2p overlap populations for the nonrelativistic case are about one-third of those for the relativistic one. The relativistic U 5f atomic orbital is expanded in comparison with the nonrelativistic one and can overlap much more with the F 2s,2p atomic orbitals. The antibonding interactions are attributed to the U 6s,6p−F 2s,2p interactions. In the nonrelativistic calculations, the $\mathbf{P_B}$ values of the U 6s−F 2s,2p and U6p−F 2s,2p antibonding interactions are −0.45 and −1.20, while they are −0.29 and −1.16 in the relativistic case. The large decrease in the U 6s−F 2s,2p antibonding interactions is due to the U 6s orbital contraction. Both relativistic contraction of the U 6s atomic orbital and relativistic expansion of the U 5f atomic orbital increase the bond overlap populations. This relativistic increase in the bond strength has also been discussed for UF_6.[9] Consequently, the relativistic calculation is important for the study of the electronic structure and chemical bonding of UF_5, although there has been a report on a nonrelativistic Xα scattered-wave calculation.[29] The relativistic calculation demonstrates that not only the U 6d atomic orbital but also the U 5f one effectively contributes to the U−F bonding.

Table 2 shows the orbital populations of the uranium and fluorine valence atomic orbitals and the effective charges on both atoms for the nonrelativistic and relativistic calculations. It can be seen that the effective charges on the ligand fluorine atoms of UF_5 are equal to those of UF_6 in the relativistic calculations, which is consistent with the result of a previous report.[5] On the other hand, the nonrelativistic calculations provide smaller effective charges and the amount of electron transfer from the uranium neutral atom to the ligand fluorine atoms is smaller than that for the relativistic calculation. The decrease in the negative charges on the fluorine atoms is mainly due to the decrease in the F 2p orbital populations. The decrease in the positive charge on the uranium atom is mainly due to the increase in the U 5f orbital population. Other valence orbital populations of the uranium atom slightly change in the opposite direction. Consequently, the differences in the U and F effective charges between the nonrelativistic and relativistic calculations arise from the change in the U 5f−F2p charge transfer. This change is attributed to the large energy difference between the U 5f and F 2p atomic orbitals due to the indirect relativistic effect in which the relativistic contraction of the inner-shell orbitals induces the upward shift in energy of the U 5f atomic orbital. Indeed, the one-electron energy, which represents the eigenvalues of atomic orbitals in a molecular potential, of the nonrelativistic U 5f atomic orbital in the UF_5 molecular potential was −7.79 eV, while those of the relativistic U $5f_{5/2}$ and U $5f_{7/2}$ AOs were −6.86 and −6.07 eV, respectively. The increase in the U 5f orbital energy effectively causes the U 5f−F2p charge transfer, because the one-electron orbital energy in the Xα method[30] is equal to the negative electronegativity. Namely, the higher energy of the relativistic U 5f orbital results in the larger amount of electron transfer.

Table 2. Orbital Populations of Valence Atomic Orbitals and Effective Charge on Uranium and Fluorine Atoms for UF_5 and UF_6

		orbital population		
atom	orbital	rel	nonrel	UF_6[a] rel
U	$5f_{5/2}$	1.81	3.80 (5f)	1.24
	$5f_{7/2}$	1.24		1.27
	$6s_{1/2}$	1.99	1.98 (6s)	1.99
	$6p_{1/2}$	1.98	5.72 (6p)	1.98
	$6p_{3/2}$	3.90		3.88
	$6d_{3/2}$	0.67	1.34 (6d)	0.77
	$6d_{5/2}$	0.90		1.06
	$7s_{1/2}$	0.08	0.04 (7s)	0.11
	$7p_{1/2}$	0.10	0.18 (7p)	0.11
	$7p_{3/2}$	0.16		0.18
eff charge		+1.16	+0.94	+1.39
F_{eq}	$2s_{1/2}$	1.93	1.95 (2s)	1.94
	$2p_{1/2}$	1.78	5.24 (2p)	1.78
	$2p_{3/2}$	3.52		3.52
eff charge		-0.23	−0.19	−0.23
F_{ax}	$2s_{1/2}$	1.92	1.94 (2s)	1.94
	$2p_{1/2}$	1.78	5.25 (2p)	1.78
	$2p_{3/2}$	3.53		3.52
eff charge		−0.23	−0.19	−0.23

[a] Reference 9.

IV. Comparison of Bond Nature between C_{4v} and D_{3h} Geometries

In order to compare the bond nature of UF_5 between the C_{4v} and D_{3h} geometries, we examined the valence level structure of UF_5 for both geometries. Tables 3 and 4 show the one-electron energies and orbital components for each valence MO, where the double group notation "γ" was first used by Bethe when he introduced the idea of the double group symmetry.[26] It was found that the electronic structure of UF_5 with D_{3h} geometry is very close to that of UF_5 with C_{4v} geometry with respect to the one-electron energies and orbital components. For example, the one-electron energy (−5.80 eV) and atomic orbital components (U 5f 94%) of the highest occupied molecular orbital (HOMO), $30\gamma_7$, for the UF_5 monomer with C_{4v} geometry is very close to those (one-electron energy, −5.72 eV; atomic orbital components, U 5f 90%) of the HOMO, $21\gamma_9$, for the monomer with D_{3h} geometry. From a comparison of the other MOs between both geometries, the valence level structures for both geometries are almost equivalent.

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Table 3. One-Electron Energies and Orbital Components for Each Valence MO of UF_5 with C_{4v} Geometry

		U (%)										F_{eq} (%)			F_{ax} (%)		
MO	energy (eV)	$5f_{5/2}$	$5f_{7/2}$	$6s_{1/2}$	$6p_{1/2}$	$6p_{3/2}$	$6d_{3/2}$	$6d_{5/2}$	$7s_{1/2}$	$7p_{1/2}$	$7p_{3/2}$	$2s_{1/2}$	$2p_{1/2}$	$2p_{3/2}$	$2s_{1/2}$	$2p_{1/2}$	$2p_{3/2}$
$32_{\gamma7}$	−4.70	17.9	68.3			0.1		1.5			0.1		0.2	10.5			1.6
$31_{\gamma7}$	−4.75	41.4	42.5			0.1	0.6	0.2					3.5	9.7			2.0
$40_{\gamma6}$	−5.42	73.6	4.3			0.1	2.7	1.0	6.8	0.4	0.2		0.7	5.9		0.2	4.2
$30_{\gamma7}{}^{a}$	−5.80	78.8	15.5				0.6	0.7					0.3	3.2			0.9
$29_{\gamma7}$	−8.66	3.9	1.3			7.5					0.4		43.8	24.1			19.1
$39_{\gamma6}$	−8.94	0.6	1.0		0.1	6.0	0.3	0.3	0.1	0.1	0.3	0.1	16.3	44.7	0.1	27.2	2.8
$38_{\gamma6}$	−9.38												31.7	68.2			
$37_{\gamma6}$	−9.72	0.2			1.4	0.1	0.1		0.1	1.1		0.3	3.4	56.0	0.4		37.1
$28_{\gamma7}$	−10.21	5.0	7.5					0.3					16.7	44.0			26.5
$36_{\gamma6}$	−10.24	6.1	6.4				0.3	0.1		0.1			27.7	37.8		16.9	4.7
$27_{\gamma7}$	−10.37	4.9	6.9				0.6	0.9				0.1	27.2	59.4			
$35_{\gamma6}$	−10.68	0.8	13.2	0.1	0.1	0.4		1.2	0.1	0.4	0.4	0.7	41.5	38.7		2.2	0.3
$34_{\gamma6}$	−10.71	2.5	2.8	0.4	0.2		1.4	0.6	0.5	0.2		2.1	28.1	60.4		0.1	0.8
$26_{\gamma7}$	−10.73	16.9	2.9			0.6		0.3			1.1	0.3	10.5	63.0			4.3
$25_{\gamma7}$	−10.95	0.7	0.7			0.2	2.2	12.5			0.3	0.3	15.6	29.2			38.2
$33_{\gamma6}$	−10.99	0.2	4.1		0.2		2.8	8.0		0.9		0.3	18.0	24.2	0.6	40.8	
$32_{\gamma6}$	−11.05	5.6	1.9			0.4	8.8			0.2	1.2	0.1	9.2	32.6	1.1		39.0
$24_{\gamma7}$	−11.26	0.9	1.7				2.4	8.2				2.1	47.0	37.7			0.1
$23_{\gamma7}$	−11.37	1.5	0.9				8.4	3.6				2.0	12.0	71.5			0.1
$22_{\gamma7}$	−21.66	0.3	0.1			66.6	0.1	0.2			2.7	23.2	3.3	3.1			0.4
$31_{\gamma6}$	−21.94	0.2	0.1			72.2	0.7	0.3			2.0	10.2	1.4	2.0	9.0	1.1	0.8
$30_{\gamma6}$	−27.30	1.1	19.7		19.7	0.5		1.6		2.3		52.2			22.8		
$29_{\gamma6}$	−28.65	0.3	0.4	1.0			0.2	0.4	3.1			81.6	0.3	0.6	12.0		
$21_{\gamma7}$	−29.03	0.2	0.3				3.2	4.7				90.6	0.4	0.7			
$28_{\gamma6}$	−30.08	0.3	0.3		0.2	18.2	1.7	1.0				29.9	0.4	0.6	45.9	0.7	1.0
$20_{\gamma7}$	−30.31	0.7	0.4			22.1	0.1	0.3				73.8	1.3	1.6			
$27_{\gamma6}$	−33.82	0.2	77.4		77.4	0.1		0.2				15.6	0.3	2.1	3.9	0.1	0.6

[a] HOMO.

Table 4. One-Electron Energies and Orbital Components for Each MO of UF_5 with D_{3h} Geometry

		U (%)										F_{eq} (%)			F_{ax} (%)		
MO	energy (eV)	$5f_{5/2}$	$5f_{7/2}$	$6s_{1/2}$	$6p_{1/2}$	$6p_{3/2}$	$6d_{3/2}$	$6d_{5/2}$	$7s_{1/2}$	$7p_{1/2}$	$7p_{3/2}$	$2s_{1/2}$	$2p_{1/2}$	$2p_{3/2}$	$2s_{1/2}$	$2p_{1/2}$	$2p_{3/2}$
$25_{\gamma8}$	−4.68	61.3	16.8			0.4		1.8		0.1		0.1		6.7		3.1	9.8
$26_{\gamma7}$	−4.93	0.4	86.7					2.6	5.0				2.8	2.1		0.5	
$25_{\gamma7}$	−5.53	72.5	9.4				2.2	0.3	6.23				0.4	8.5		0.1	0.4
$21_{\gamma9}{}^{a}$	−5.72	82.0	8.0				0.8	0.9					0.4	6.0			1.9
$24_{\gamma8}$	−8.76	3.8	0.7			7.1					0.5		14.9	40.4	0.1	24.1	8.5
$20_{\gamma9}$	−8.83	0.5	0.6			6.5	0.2				0.4	0.1	49.9	26.3			15.5
$23_{\gamma8}$	−9.69	0.2	0.5		1.4					1.3		0.4	4.1	73.5	0.1		18.6
$19_{\gamma9}$	−9.77	4.4	1.6										18.7	34.0			41.3
$24_{\gamma7}$	−9.77	0.7	4.5										16.5	38.3		26.0	14.0
$23_{\gamma7}$	−10.49	8.3	9.9										30.8	50.9		0.2	
$22_{\gamma9}$	−10.53	1.0	4.7		0.1	0.3		7.3			0.2	0.3	19.0	37.7		24.2	5.3
$18_{\gamma9}$	−10.53	2.4	4.4			0.2	5.8	1.6			0.1	0.2	7.7	43.4			33.8
$21_{\gamma8}$	−10.77	11.1	8.7		0.4	0.9		0.5		0.4	0.7	0.1	27.2	15.1	0.6	5.2	29.2
$22_{\gamma7}$	−10.81	3.8	2.9	0.5			0.1	0.2	0.7			1.4	15.9	36.0	0.9	13.2	24.5
$17_{\gamma9}$	−10.97	2.8	6.6			0.5	3.8	1.9			1.6	1.0	1.6	41.4			38.8
$20_{\gamma8}$	−10.98	7.7	3.9		0.1	0.2		3.9		1.1	0.6	0.9	22.1	15.2		28.8	15.6
$16_{\gamma9}$	−11.31	1.7	0.3				4.8	11.9					10.8	22.9			47.7
$21_{\gamma7}$	−11.34		1.7				6.3	9.1				0.2	18.4	14.0	0.2	46.7	3.5
$20_{\gamma7}$	−11.47	1.8	1.1				6.8	0.1				1.6	4.1	29.1	2.3	4.8	48.3
$19_{\gamma8}$	−21.68	0.3	0.1			66.6		0.4			2.6	5.7	0.8	1.4	17.2	2.7	2.2
$15_{\gamma9}$	−21.91		0.1			71.5	1.0	0.2			2.1	19.6	2.6	2.1			0.7
$18_{\gamma8}$	−27.27		0.8		19.6	0.1		2.0		2.3		53.3			22.1		
$19_{\gamma7}$	−28.60	0.6	0.9	0.9			0.1	0.2	2.9			81.5	0.3	0.6	12.0		0.1
$18_{\gamma7}$	−29.21	0.1	0.1	0.1			3.2	4.6	0.3			11.1	0.1	0.1	79.3	0.3	0.6
$14_{\gamma9}$	−30.00	0.1	0.3			19.4	1.9	0.5				75.5	1.1	1.5			0.1
$17_{\gamma8}$	−30.43	0.8	0.3		0.9	21.7		0.8				25.8	0.5	0.7	47.2	0.8	0.8
$16_{\gamma8}$	−33.87				76.7	0.2		0.2				9.7	0.2	1.4	10.3	0.2	1.2

[a] HOMO.

When two of the F_{eq} atoms in the D_{3h} geometry (see Figure 1) are slightly rotated by 9° toward the other F_{eq} atoms, the F_{ax} atoms are slightly rotated by 11° opposite to the fixed F_{eq} atom and the D_{3h} geometry converts to the C_{4v} geometry through the C_{2v} geometry. Since these geometries are similar to each other, the barrier of the transition between the C_{4v} and D_{3h} geometries through the C_{2v} geometry is expected to be small. In order to confirm this prediction, we examined the stability in bonding for the C_{4v} and D_{3h} geometries in terms of bond overlap populations between the uranium and fluorine atoms.

Table 5 summarizes the results of the bond overlap populations, orbital populations, and effective charges on the uranium and ligand fluorine atoms for these structures, together with previous theoretical results.[5] Since the bond overlap population of 1.79 for the C_{4v} geometry is almost equal to that of 1.77 for the D_{3h} geometry, the two geometries are essentially equivalent

Table 5. Comparison of Orbital Populations, Effective Charges of Uranium and Fluorine Atoms, and Bond Overlap Populations between C_{4v}, D_{3h}, and C_{2v} Geometries Compared with Those of a Previous Study[5]

		orbital population					
		present study				previous study[5]	
atom	orbital	C_{4v}[a]	D_{3h}[b]	C_{2v}[c]		C_{4v}[d]	D_{3h}[b]
U	$5f_{5/2}$	1.81	1.86	1.82	f	1.97	1.94
	$5f_{7/2}$	1.24	1.18	1.26			
	$6s_{1/2}$	1.99	1.99	1.99	s	2.18	2.18
	$6p_{1/2}$	1.98	1.98	1.98	p	6.31	6.30
	$6p_{3/2}$	3.90	3.90	3.89			
	$6d_{3/2}$	0.67	0.69	0.66	d	1.18	1.20
	$6d_{5/2}$	0.90	0.91	0.89			
	$7s_{1/2}$	0.08	0.08	0.09			
	$7p_{1/2}$	0.10	0.10	0.09			
	$7p_{3/2}$	0.16	0.16	0.16			
	eff charge	1.16	1.15	1.17		2.36	2.38
F_{eq}	$2s_{1/2}$	1.93	1.93	1.93	s	1.94	1.93
	$2p_{1/2}$	1.78	1.78	1.78	p	5.54	5.55
	$2p_{3/2}$	3.52	3.53	3.52			
	eff charge	−0.23	−0.24	−0.24		−0.48	−0.46
F_{ax}	$2s_{1/2}$	1.92	1.93	1.93	s	1.94	1.94
	$2p_{1/2}$	1.78	1.77	1.78	p	5.54	5.53
	$2p_{3/2}$	3.53	3.51	3.52			
	eff charge	-0.23	−0.21	−0.22		−0.48	−0.47
bond overlap population		1.79	1.77	1.79			

[a] $U-F_{ax} = 2.00$ Å, $U-F_{eq} = 2.02$ Å, $F_{ax}-U-F_{eq} = 101°$.[1] [b] $U-F_{ax} = 1.99$ Å, $U-F_{eq} = 2.02$ Å, $F_{ax}-U-F_{eq} = 90°$.[5] [c] $U-F_{ax} = 2.00$ Å, $U-F_{eq} = 2.02$ Å, $F_{ax}-U-F_{eq} = 90°$, $F_{eq}-U-F_{eq} = 101°$. (intermediate between C_{4v} and D_{3h}). [d] $U-F_{ax} = 2.00$ Å, $U-F_{eq} = 2.00$ Å, $F_{ax}-U-F_{eq} = 100°$.[5]

in bonding stability. Even in the orbital populations and the effective charges on the atoms, the C_{4v} geometry differs little from the D_{3h} geometry. In a comparison of the present results with previous ones, it is found that the populations of ligand fluorine atomic orbitals are similar. In contrast, those of uranium atomic orbitals, especially the U 6d and U 5f atomic orbitals which are affected by the indirect relativistic effect, are quite different. This discrepancy may be due to the relativistic effective core potential approximation used by Wadt and Hay.[5]

We next examined the electronic structure of UF_5 with the C_{2v} intermediate geometry (two $F_{eq}-U-F_{eq}$ bond angles in the D_{3h} geometry are reduced from 120 to 101°) between the C_{4v} and D_{3h} geometries. Table 5 shows the results for the intermediate geometry along with those for the C_{4v} and D_{3h} geometries. The effective charges on the equatorial and axial fluorine atoms are −0.24 and −0.22, respectively, and that on the uranium atom is +1.17. The bond overlap population of the C_{2v} intermediate geometry is +1.79. These values are almost equal to those of the C_{4v} and D_{3h} geometries. In addition, the one-electron energies and orbital components for the C_{2v} geometry are similar to those for the other geometries. These findings suggest that the energy barrier between the C_{4v} and D_{3h} geometry is very small and both geometries are interconvertible. Consequently, the results of the present study agree with the previous theoretical result[5] that the gaseous UF_5 monomer fluctuates between C_{4v} and D_{3h} geometries. Unfortunately, it is difficult to confirm this theoretical prediction experimentally at the present stage.

On the basis of the above results obtained by the bond overlap population analysis, we attempt to interpret the origin of the fluxional structure of the UF_5 monomer qualitatively. Studies on the difference in theoretical energies (ΔE) between the C_{4v} and D_{3h} geometries for other pentafluorides such as SF_5[31,32] and PF_5 have been reported.[33,34] The ΔE values for SF_5 and PF_5 are estimated to be 0.90−1.57 and 0.18−0.21 eV, respectively. On the other hand, the ΔE for UF_5 is reported to be 0.04 eV.[5] Thus, it can be seen in terms of energy that UF_5 is more fluxional between the two geometries than the other pentafluorides. This fluxional geometry originates from the fact that the U 5f atomic orbital plays a major role in the U−F bonding and has a wide angular distributions resulting in the flexibility of the bond angle in hybridization with the U 6d atomic orbital. This cannot be explained in the framework of nonrelativistic calculations, because the U 5f electrons play a minor role in the chemical bonding in the nonrelativistic case.

Finally, we evaluated the first ionization potential (IP) of the UF_5 monomer with the C_{4v} experimental geometry using Slater's transition method[35] and obtained an IP value of 9.8 eV. The present result provides almost the same value as that of 9.7 eV reported by Rosén and Fricke,[4] who examined the D_{4h} geometry of the UF_5 monomer using the DV-DS method, and is in reasonable agreement with the experimental value of 11.29 eV.[36]

V. Summary

We performed relativistic and nonrelativistic calculations for the UF_5 monomer with the C_{4v} and D_{3h} geometries, using the nonrelativistic and relativistic DV-Xα MO method. The following conclusions are obtained.

(1) On examining bond overlap populations between the uranium and fluorine atoms, we found that the relativistic effects are of great importance in the chemical bonding of molecules containing heavy elements such as uranium. In particular, it is interesting to note that the U 5f electrons mainly participate in U−F bonding interactions similar to the U 6d electrons.

(2) We compared the structural stability of the C_{4v} and D_{3h} geometries for UF_5 in terms of the bond overlap population analysis. The electronic structure of UF_5 is almost constant even with the bond angle variation from the C_{4v} geometry to the D_{3h} geometry through the C_{2v} intermediate geometry. This supports the conclusion of the previous study that the UF_5 monomer fluctuates between the C_{4v} and D_{3h} geometries. The origin of the structural flexibility of the UF_5 monomer is that the U 5f atomic orbitals, which play a major role in U−F bonding, have wide angular distributions of the electrons in hybridization with the U 6d atomic orbital.

Finally, the valence level structure consists of the 5f, 6s, 6p, 6d, and 7s atomic orbitals in uranium atom. This means that s-, p-, d-, and f-electrons can participate in the chemical bonding of uranium compounds. Thus, hybridization of those atomic orbitals gives rise to a variety of bond numbers in the compounds, and in particular, that of the U 5f and U 6d atomic orbitals leads to a bond flexibility against the change in geometry.

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