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Recent Developments in the Theory of f-Element Molecules*

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Abstract

The available relativistic calculations on f-element molecules are briefly reviewed. The role of the 6p semicore orbitals in the actinoids is underlined. In fact, the 6p hole in actinyls is suggested to give the main contribution to the actinoid nuclear quadrupole coupling in $^{234}UO_2^{2+}$ or $^{237}NpO_2^{2+}$. The $^1J(U–F)$ spin–spin coupling constant in UF_6 is calculated to be small.

Introduction

The available relativistic calculations on atoms and molecules have recently been reviewed [1]. About 60 calculations on molecules containing lanthanoids and actinoids are summarized in Table I. Extended Hueckel-level calculations on reaction pathways [2] are not included as they have been reviewed separately by Tatsumi and Nakamura [3]. For earlier reviews, see refs. 18, 61–64.

Magnetic Resonance Parameters

Nuclear Quadrupole Coupling

The early 5f elements are also '6p elements', in the sense that the $6p_{3/2}$ AO hybridises with ligand AOs, and does not remain fully occupied [7–9, 21, 27, 49, 52–53, 55–56, 58, 63–65]. This hybridization is particularly large in uranyl and the other actinyls. The corresponding 6p hole is about 0.1–0.3 e, depending on R and the method of calculation [56]. Direct experimental evidence for U(6p)–O(2s) hybridization in uranyl compounds is provided by the X-ray photoemission spectra by Veal *et al.* [66] and by the ^{235}U internal conversion spectra [67].

Because the 6p $\langle r^{-3}\rangle$ integral is much larger than the 6d or 5f ones (80.61, 4.52 and 5.71 a.u., for $6p_{3/2}$, $6d_{3/2}$ and $5f_{5/2}$, respectively [68]), it was suggested in ref. 56 that the main contribution to the

TABLE I. Relativistic Calculations on Molecules Containing f-Elements (classified by method of calculation and, for each method, in chronological order)

Method	Molecule(s)	Properties^n	Ref.
DF-OCE^a	CeH_4, ThH_4, UH_6	R, k	4
DF-OCE	MH^+, MH_2 (M = Yb, No)	R, k	5
DF-OCE	MH (M = Sc, Y, La, Ac, Tm, Lu, Lr)	R, k	6
DS-DVM^b	UO_2^{2+}	B	7
DS-DVM	AnF_6 (An = U–Pu)	E_i, B	8
DS-DVM	UO_2^{2+} (in a crystal field)	E_i, B	9
DS-DVM	UO_6^{10-}	E_i	10
DS-DVM	UF_6	E_i, UV	11
DS-DVM	UF_6	B	12
DS-DVM	ThO_6^{10-}, UO_6^{10-}	B	13, 14
DS-DVM	UF_5	E_i, UV	15
DS-DVM	AnF_4 (An = Th, U–Pu), UO_4^{Q-}	PES, UV, B	16
DS-DVM	LnX_3	PES	17, 18
DS-DVM	AnO_8^{12-} (An = U–Cm)	B	18
DS-DVM	TmS_n	E_i	19
DS-DVM	AnX_4 (An = U–Pu)	E_i, B	20
DS-MS^c	UO_2^{2+}	PES	21
DS-MS	UF_6	E_i	22
DS-MS	YbF_6^{3-}, YbF_8^{5-}	hfs	23
DS-MS	NpF_6	hfs, g	24
DS-MS	UF_6	E_i, B	25
QR-MS^d	UF_6	E_i, B	26, 27
QR-MS	UO_2^{2+}	B	27
QR-MS	UCl_6	PES	28
QR-MS	PaX_6^{2-}, UX_6^-, NpF_6 (X = F–I)	UV, B	29
QR-MS	UO_2^{n+} (n = 0–2)	UV, B	30
QR-MS	$(cp)_2UX_2$ (X = Cl, CH_3)^e	PES, B	31
QR-MS	UO_8^{n-}	E_i, B, IS	32
QR-MS	$M(cot)_2^f$	UV, PES, B	33, 34
QR-MS	UF_4	E_i, UV, PES, EA	35
QR-MS	$An(cp)_4$ (An = Th, U)	PES, B	36
QR-MS	UCl_4, $U(cp)_4$, $UCl_2(cp)_2$	B	37
QR-MS	NpF_6	hfs	24
QR-MS	$Ce(cot)_2$	PES	38

(continued)

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TABLE I. *(continued)*

Method	Molecule(s)	Properties^n	Ref.
QR-MS^d	$An(BH_4)_4$ (An = Th, U)	PES, B	39
QR-MS	$(cp)_2ITh-Ru(cp)(CO)_2$	B	40
PP^g	$UF_6^{0,+,-}$	R, PES, UV	41
PP	UF_5	G, UV	42
PP	ThO_2, UO_2^{2+}	G, B	43
PP	UF_6	UV	44
PP	$UH^{0,+,-}$, $UF^{0,-}$	R, k	45
PP	UO, UO^+	R, k	46
PP	$Cl_2Th(\mu\text{-}PH_2)Pt(PH_3)$	B	47
PP	PuF_6	UV	48
P-HFS^h	UO_2^{2+}	E_i, B	49
P-HFS	$An(cot)_2$ (An = Th–Pu)	E_i, B, R	76
P-HFS	AnX_4 (An = Th, U; X = F, Cl)	E_i, B, R	76
EHT^i	UO_2^{2+}	B	50
EHT	$An(cot)_2$	B	51
EHT	UO_2^{2+}	B, G	52
REX^j	UO_2^{2+}, $UO_2Cl_4^{2-}$, UX_6, UCl_4, $U(BH_4)_4$, $U(cot)_2$,	E_i, B	53
	LnI_3 (Ln = La, Gd, Lu)	B, G	
REX	UF_6	E_i, B, ESCA	54
REX	UO_2^{2+}	E_i, B	55
REX	UF_6, UO_2^{2+}, $UO_2X_4^{2-}$	E_i, Q	56
REX	LnX_3 (Ln = La, Nd, Gd, Lu, X = F–I)	E_i	57
GN^k	UO_2^{2+}	B	58bc
BL^l	$UO_2X_n^{m-}$	E_i	59
INDO^m	$(cp)_2Lu(Cl)OC_4H_8$	E_i, B	60

[a] Dirac–Fock One-Centre Expansion. [b] Dirac–Slater Discrete Variational Method. Fock stands for full, non-local exchange while Slater stands for a local exchange approximation. [c] Dirac-Slater Multiple-Scattering. [d] Quasirelativistic (one-component) Multiple-Scattering. [e] cp = C_5H_5. [f] cot = C_8H_8. [g] Pseudopotential. [h] Perturbative Hartree–Fock–Slater. [i] Extended Hueckel Theory with averaged relativistic parameters. [j] Relativistic Extended Hueckel (including spin–orbit splitting). [k] A CNDO-level method with spin–orbit splitting but NR radial functions. [l] EHT + spin–orbit. [m] Intermediate Neglect of Differential Overlap. [n] R = bond lengths, G = geometry, k = force constants, ESCA = shake-up spectra, B = bonding, UV = optical/UV spectrum, hfs = magnetic hyperfine structure, g = g-tensors, PES = photoelectron spectrum, IS = Mössbauer isomer shifts, EA = electron affinity, Q = nuclear quadrupole coupling.

nuclear quadrupole coupling constant (NQCC) in $^{234}UO_2^{2+}$ or $^{237}NpO_2^{2+}$ could actually come from this source. Further evidence is provided by the increase of NQCC with decreasing R.

Nuclear Spin–Spin Coupling

Although ^{235}U NMR signals have been seen in UF_6 [69], no splittings due to the $^1J(UF)$ spin–spin coupling were observed. Ursu *et al.* [70] claim to have seen ^{235}U-induced relaxation processes in UF_6 but do not report a value for the spin–spin coupling constant. Similarly, Seppelt and Bartlett [75] saw a ^{19}F line broadening in $^{235}UF_6$, but no resolved splittings.

A REX-level calculation [71] suggests that the $^1J(UF)$ would be small; the calculated value is only -110 Hz.

No $^1J(UO)$ was observed in $^{235}U^{17}O_2^{2+}$ solutions, either, perhaps due to fast uranium quadrupole relaxation [72–73].

NMR Chemical Shifts

The ^{19}F chemical shift in $UF_6(s)$ is strongly 'paramagnetic' (-734 ppm downfield from gaseous F_2 [74]), mainly due to the perpendicular component ($\sigma_\parallel = +73$, $\sigma_\perp = -1137$, $\sigma_\parallel - \sigma_\perp = 1210(30)$ ppm [74]).

The ^{17}O shifts in uranyl also are among the most paramagnetic ones for oxygen, or around -1130 ppm downfield from H_2O [72].

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