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surface layer of oxide formed on PuO_xC_y by oxidizing gases is apparently very coherent and functions as an effective diffusion barrier against extensive reaction.

A dearth of thermochemical data has long hindered resolution of questions about the existence of condensed PuO. Although that situation is not directly improved by the results of this study, the thermodynamic values estimated for PuO[5] definitely cannot be applied to PuO_xC_y. Only the C_p values and the enthalpy increments estimated for the monoxide are valid. Since data are insufficient for a Born-Haber calculation, enthalpy of formation estimates have been used on the analogy of PuO_xC_y to $SmO_{0.51}C_{0.38}$ and to PuN. Since the compositions of the Sm and Pu phases are virtually identical, $\Delta H_f°_{298}[PuO_xC_y(s)]$ should be similar to the -370 kJ mol^{-1} value of samarium oxide carbide.[25] Plutonium nitride is isostructural and isoelectronic with the oxide carbide, and $\Delta H_f°_{298}[PuN(s)] = -317$ kJ mol^{-1}.[5] The average estimated $\Delta H_f°_{298}[PuO_xC_y(s)]$ obtained from the values for these model phases is -344 ± 35 kJ mol^{-1}. $S°_{298}[PuO_xC_y(s)]$ has been obtained with use of Latimer's method with lattice contributions of 67, 0, and -16 J K^{-1} mol^{-1} for Pu, O, and C.[25-27] Inclusion of a magnetic contribution similar to that of trivalent samarium (14.6 J K^{-1} mol^{-1})[27] gives an estimated $S°_{298}[PuO_xC_y(s)]$ of 75 J K^{-1} mol^{-1} and in conjunction with $S°_{298}$ data for the elements[5,28] leads to values of $\Delta S_f°_{298}[PuO_xC_y(s)] = -33 \pm 5$ J K^{-1} mol^{-1} and $\Delta G_f°_{298}[PuO_xC_y(s)] = -334 \pm 38$ kJ mol^{-1}.

The thermodynamic estimates are consistent with the reactions observed in this study. As previous investigators have noted, PuO should be thermodynamically unstable relative to Pu_2O_3 and Pu.[3] However, $\Delta G°_{298}$ for the formation of PuO_xC_y according to eq 1 is -63 kJ mol^{-1}. This result, which is derived

$$0.17Pu_2O_3(s) + 0.67Pu(s) + 0.40C(s) \rightarrow PuO_{0.5}C_{0.4}(s) \qquad (1)$$

from the estimated $\Delta G_f°_{298}$ of $PuO_xC_y(s)$ and from that of Pu_2O_3,[5] supports our conclusions that the NaCl-type surface phase is the stable oxide carbide and that its thickness is determined by the availability of carbon. The data are also consistent with the proposed formation of a transient plutonium carbide phase that ultimately reacts to form PuO_xC_y. Free energy calculations for the reaction of known carbides with the oxide and metal show that all possible processes are spontaneous.

The reactions of PuO_xC_y with CO, CO_2, and O_2 to form $PuO_2(s)$ plus C(s) are also spontaneous. The least favorable of these processes is given by eq 2 and has $\Delta G°_{298} = -373$ kJ

$$PuO_{0.5}C_{0.4}(s) + 0.75CO_2(g) \rightarrow PuO_2(s) + 1.15C(s) \qquad (2)$$

mol^{-1}.[5,28] The ΔG_{298} values for eq 2 with the partial pressures that were present during CO_2 treatment (1.3 Pa) and during exposure to residual CO_2 (10 nPa) are -360 and -297 kJ mol^{-1}, respectively. Equation 2 and the parallel reaction for CO are particularly important because they provide a mechanism for increasing the surface concentration of carbon on plutonium.

The present study supports a Pu-O phase diagram in which the condensed monoxide does not exist at standard conditions. However, recent studies with the rare earths at high pressures (40-80 GPa) and high temperatures (600-1200 °C) show that several elements (La-Nd, Sm) react with their higher oxides to form metallic NaCl-type monoxides and that Yb forms a nonmetallic monoxide.[29] These rare earths are similar to Pu in that their condensed monoxides are unstable at standard conditions. Although the known high-temperature surface phase is definitely PuO_xC_y, it is reasonable to assume that the synthesis of PuO can be achieved by similar high-pressure techniques.

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Registry No. Pu, 7440-07-5; O_2, 7782-44-7; PuO_2, 12059-95-9; α-Pu_2O_3, 12036-34-9; PuO, 12035-83-5; PuC, 12070-03-0; CO, 630-08-0; CO_2, 124-38-9.

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(25) Haschke, J. M., to be submitted for publication.
(26) Latimer, W. M. *J. Am. Chem. Soc.* **1951**, *73*, 1480.
(27) Westrum, E. F., Jr. *Adv. Chem. Ser.* **1967**, *No. 71*, p 25.
(28) "JANF Thermochemical Tables", *Natl. Stand. Ref. Data Ser.* (*U.S. Natl. Bur. Stand.*) **1971**, *NSRDS-NBS 37*.
(29) Leger, J. M.; Yacoubic, N.; Loriers, J. "The Rare Earths in Modern Science and Technology"; Plenum Press: New York, 1980; Vol. 2, p 203.

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Relativistically Parameterized Extended Hückel Calculations. 3. Structure and Bonding for Some Compounds of Uranium and Other Heavy Elements

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The relativistically parameterized extended Hückel molecular orbital method REX is used to explore the effects of relativity upon molecular orbital energies and compositions. The uranium compounds studied are UO_2^{2+}, $UO_2Cl_4^{2-}$, UF_6, UCl_6, UCl_4, $U(BH_4)_4$, and $U(C_8H_8)_2$. Other heavy element compounds studied are MI_3 (M = La, Gd, Lu), PoH_2, (eka)PoH_2, I_3^-, AtI_2^-, and RnF_2. Relativistic orbital energy parameters and atomic orbital exponents are presented as supplementary material for all elements with $Z = 1-120$ together with corresponding nonrelativistic values for all elements with $Z = 1-100$. It is concluded that the REX method provides semiquantitative estimates of spin-orbit splittings and relativistic bonding effects for compounds of heavy elements.

Introduction

In a recent publication,[1] referred to hereafter as part 1, we outlined a relativistically parameterized version of extended Hückel theory (EHT) called REX. This method incorporates relativistic effects by its use of atomic orbital basis sets with an $|lsjm\rangle$ quantization and by its systematic parameterizations based on Desclaux' atomic relativistic Dirac-Fock (DF) and nonrelativistic Hartree-Fock (HF) calculations.[2] No spin-orbit Hamiltonian need be specified, as the diagonal Hamil-

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(1) L. L. Lohr, Jr., and P. Pyykkö, *Chem. Phys. Lett.*, **62**, 333 (1979).
(2) J. P. Desclaux, *At. Data Nucl. Data Tables*, **12**, 311 (1973).

tonian matrix elements in the $|lsjm\rangle$ basis are taken as the DF atomic orbital energies and the off-diagonal elements are taken to be proportional to the product of the overlap matrix element in the $|lsjm\rangle$ basis and the arithmetic mean of the corresponding diagonal elements. In its simplest form, REX employs single Slater atomic basis functions, with exponents ζ obtained by a fit to DF electron mean radii. The alternative use of ζ's, fit to HF mean radii, and of HF orbital energies provides the nonrelativistic reference calculation. We have also developed a multi-ζ version of REX and presented[3] in part 2 the results of its use in a study of orbital energies of group 4 tetrahalides and tetramethyls. In addition, we have made the REX FORTRAN program available for general use.[4]

In part 1 we compared[1] our method to the closely related but less general procedure[5] of Manne, Wittel, and Mohanty. Reference was also made to other less general semiempirical relativistic methods.[6,7] We concluded from our preliminary studies that REX with its dual parameterizations provides a semiquantitative description of relativistic effects in chemical bonding.[8] It should be noted that a number of relativistic methods of varying degree of sophistication have been used in studying molecules. These have been reviewed[9] by Pyykkö and include Dirac–Fock one center expansion (DF-OCE), Dirac–Slater discrete variational (DS-DVM), Dirac–Slater multiple scattering Xα (DS-MSXα), and relativistic pseudopotential methods. The chief advantage of REX over any of the above is its low cost making it applicable to very large systems.

Parameterization

A. Default Parameters. REX parameters for the elements 1–120 together with nonrelativistic values for the elements 1–100 are available as supplementary material referred to here as Table A. The same parameters are given as a default option in the REX program.[4] Faithful to our original philosopy in part 1, we use the Dirac–Fock (DF) or Hartree–Fock (HF) orbital energies, ϵ_i, for the diagonal Hamiltonian matrix elements $\alpha_i = h_{ii}$. The orbital exponents are mostly related to the average radii $\langle r\rangle_i$ by eq 1 where n_i is the principal quantum number.

$$\zeta_i = (n_i + 1/2)/\langle r\rangle_i \qquad (1)$$

Desclaux' average-of-configuration results[2] were used where available. For those valence orbitals that are unoccupied in the atomic ground state such as Hg(6p), we carried out analogous calculations using his program[10] and the electron configurations given in Table A. For these orbitals, marked by "M" in Table A, where eq 1 would give excessively diffuse orbitals, the radius of maximum density, r_{max}, was used:

$$\zeta_i = n_i/r_{max}{}^i \qquad (2)$$

B. Modifications. If realistic results are to be obtained for hydrides, the $h_{ii}(H)$ must be modified. For BaH_2 at $R = 2.17$ Å, the DF-OCE orbital energies for σ_g and σ_u MO's[11] can be reproduced by a $h_{ii}(H)$ of about −7 eV. The HF-LCAO orbital energies for the a_1 and t_2 MO's of TiH_4[12] can be reproduced by values of −11 and −12 eV, respectively. Anders et al.[13] used for H chemisorbed on W a value of −10 eV. The same value was used by Fassaert and van der Avoird[14] for H chemisorbed on Ni. We use a value of −10 eV for the hydrides in this study.

For the alkalies and alkaline earths, the valence np and (n − 1)d orbitals are tabulated together with the valence ns orbital. If the (n −1)p core orbitals are desired instead, parameters for them may be obtained from Desclaux' tables[2] and eq 1.

For the strongly electronegative oxygen atom, bound to uranium in $UO_2{}^{2+}$, the default α's are too low and result in a wrong order of the 2s-type 1u and 1g MO's in Figure 1. Satisfactory orbital energies are obtained by keeping the U α's unchanged while shifting the oxygen α's upward by 4 eV to −30 and −12.8 eV. This 4-eV shift also suffices to bring the orbital energies of a $PuO_8{}^{12-}$ cluster into agreement with experimental data[15] for solid PuO_2.

The same problem arises for F in UF_6. We shift the levels upward by 5 eV to −37.9, −14.901, and −14.828 eV for the 2s, $2p_{1/2}$, and $2p_{3/2}$ levels, respectively.

Due to the importance of halogen–halogen overlap, we decrease the ζ(F) values to 2.3863, 1.9721, and 1.9653 for 2s, $2p_{1/2}$, and $2p_{3/2}$ levels, respectively, corresponding to eq 1 for F^- ion.[16] For Cl we use the default α's and the double-ζ parameters of ref 3.

In the remainder of this paper we shall use the designation "REX" for calculations made with the use of relativistic parameters of Table A and the designation "EHT" for calculations made with the use of the complementary nonrelativistic parameters of Table A. Both REX and EHT calculations employ the $|lsjm\rangle$ basis.

Uranium Compounds

A. $UO_2{}^{2+}$ and $UO_2Cl_4{}^{2-}$. The first uranium compound which we consider is the familiar $UO_2{}^{2+}$ ion, which has been the subject of several recent relativistic calculations.[17-20] Using a uranium basis set consisting of 7s, 6p, 6d, and 5f AO's together with a U–O bond length of 1.71 Å,[21] we have computed the orbital energies as a function of bond angle. The total orbital energy is a minimum for a linear structure; this result obtains both with the use of default parameters (see section on default parameters) and with the use of shifted oxygen orbital energies (see section parameter modifications). Orbital energies for the linear structure are compared in Figure 1 to the DS-DVM values of Walch and Ellis.[17] The orbitals are labeled by the value of $2|m|$ and parity. The order of our five lowest MO's agrees with that of Walch and Ellis if the shifted oxygen (see section on modifications) is used. Our HOMO for $UO_2{}^{2+}$ is 1u (51.4% $5f_{5/2}$, 32.2% $5f_{7/2}$ with default parameters; 60.2% $5f_{5/2}$, 26.5% $5f_{7/2}$ with shifted oxygen parameters), as is theirs, that of Tatsumi and Hoffmann,[20] and that of Denning et al.[22] Our LUMO and that of Walch and Ellis is the nonbonding 5u (100% $5f_{5/2}$, $m = \pm 5/2$). Yang et al.[18] find a 3g HOMO but suspect that a 1u, corresponding to a nonrelativistic $3\sigma_u$, is the correct one. Their LUMO is also 5u.

---

(3) L. L. Lohr, Jr., M. Hotokka, and P. Pyykkö, *Int. J. Quantum Chem.*, **18**, 347 (1980).

(4) L. L. Lohr, Jr., M. Hotokka, and P. Pyykkö, *QCPE*, **12**, 387 (1980).

(5) R. Manne, K. Wittel, and B. S. Mohanty, *Mol. Phys.*, **29**, 485 (1975).

(6) E. A. Boudreaux, T. P. Carsey, A. Dutta-Ahmed, E. S. Elder, and L. E. Harris, Abstracts of EUCHEM Conference on Electronic Structure of Transition Metal Complexes, Maynooth, Ireland, 1978.

(7) I. B. Bersuker, S. S. Budnikov, and B. A. Leizerov, *Int. J. Quantum Chem.*, **11**, 543 (1977).

(8) Relativistic effects in chemistry have been recently described by: (a) K. S. Pitzer, *Acc. Chem. Res.*, **12**, 271 (1979); (b) P. Pyykkö and J. P. Desclaux, *ibid.*, **12**, 276 (1979).

(9) P. Pyykkö, *Adv. Quantum Chem.*, **11**, 353 (1978).

(10) J. P. Desclaux, *Comput. Phys. Commun.*, **9**, 31 (1975).

(11) P. Pyykkö, *J. Chem. Soc., Faraday Trans. 2*, **75**, 1256 (1979).

(12) M. Hotokka and P. Pyykkö, *J. Organomet. Chem.*, **174**, 289 (1979).

(13) M. W. Anders, R. S. Hansen, and L. S. Bartell, *J. Chem. Phys.*, **59**, 5277 (1973).

(14) D. J. M. Fassaert and A. van der Avoird, *Surf. Sci.*, **55**, 291 (1976).

(15) R. Baptist, private communication.

(16) J. P. Desclaux, private communication.

(17) P. F. Walch and D. E. Ellis, *J. Chem. Phys.*, **65**, 2387 (1976).

(18) C. Y. Yang, K. H. Johnson, and J. A. Horsley, *J. Chem. Phys.*, **68**, 1001 (1978).

(19) M. Boring and J. H. Wood, *J. Chem. Phys.*, **71**, 392 (1979).

(20) K. Tatsumi and R. Hoffmann, *Inorg. Chem.*, **19**, 2656 (1980).

(21) The distance in α-$UO_2(OH)_2$: J. C. Taylor, *Acta Crystallogr., Sect. B*, **B27**, 1088 (1971).

(22) R. G. Denning, T. R. Snellgrove, and D. R. Woodwark, *Mol. Phys.*, **37**, 1109 (1979).

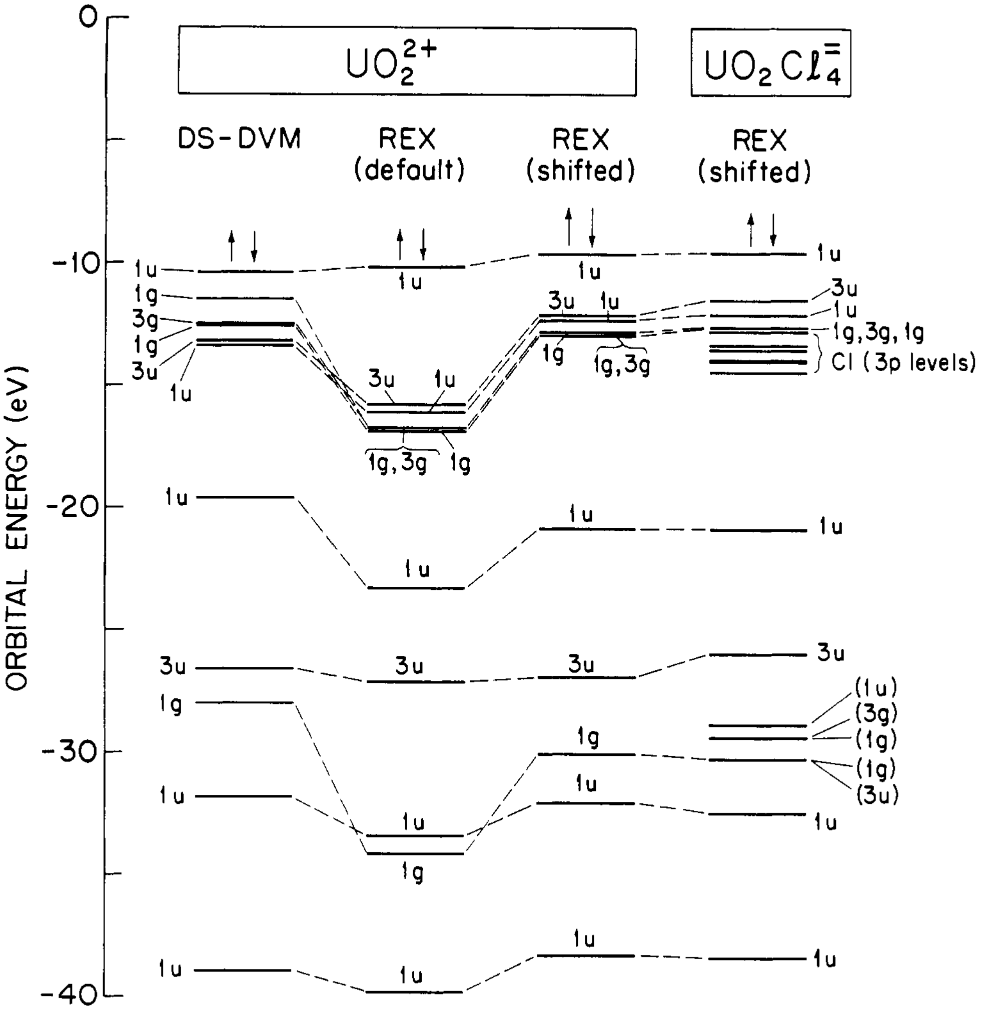

Figure 1. REX orbital energies for UO_2^{2+} and $UO_2Cl_4^{2-}$ compared to the DS-DVM values (shifted upward by 12 eV) of ref 17. The "shifted" REX values were obtained by using the shifted O parameters from the section on parameter modifications. The highest level shown is the 1u HOMO. The $D_{\infty h}$* symmetry labels denote 2|*m*| and parity.

The variation of the UO_2^{2+} orbital energies with angle is shown in Figure 2. While the O(2s), O(2p), and U(6p) AO's are strongly mixed, the sum of the first nine MO energies is nearly independent of bond angle. The linearity may be attributed in our model to the fact that the energy of the MO number 10 rises with decreasing angle. This MO is of 3u symmetry corresponding, together with the 1u MO number 9, to a nonrelativistic π_u MO. The U(6p) AO's may play a role in that while the $6p_{1/2}$ AO's are virtually isolated, and the $6p_{3/2}$ AO's, almost 10 eV higher in energy, contribute 1.8% to this 3u MO. While this π_u MO is U(6p)-O(2pπ) antibonding, it is U(5fπ)-O(2pπ) bonding. The 3u component (number 10) is 9.1% 5f. Thus we would straightforwardly attribute the linearity of UO_2^{2+} to the loss of this fπ-pπ bonding.

Since the UO_2^{2+} LUMO is nonbonding, REX also predicts linearity for neutral UO_2. Wadt et al.[23] arrive at a similar conclusion using their RXα method. Infrared studies in an Ar matrix do indeed suggest[24] linearity for UO_2, although beam deflection experiments suggest[25] nonlinearity.

We have also carried out REX calculations for the actinide MO_2^{2+} species with M = Np, Pu, and Am, using a common bond length of 1.71 Å and M(6p) AO's. "High-spin" orbital occupations were assumed for thse $5f^m$ (m = 1-3) species. All of these species were found to be linear. A discussion of the properties of some of these ions, together with the ions MO_2^{+}, MO_2^{3+}, and MO_2^{4+}, has been given by Ionova and Spytsyn.[26]

The 5f orbital participation in the boonding of the ion UO_2^{2+} corresponds to overlap populations (by using the shifted oxygen orbital energies) for $5f_{5/2}$ of 0.01 and 0.08 to 2s and 2p, respectively, of each O atom and similarly populations for $5f_{7/2}$ of 0.01 and 0.10, respectively; the sum of these is about 34% of the total overlap population of 0.59 to each O atom.

A question is whether U(7p) AO's might represent a better choice than U(6p) AO's for use in REX descriptions of uranium compounds. Tatsumi and Hoffmann[20] use both in their treatment of UO_2^{2+}. It is known that U(6p) participate strongly in bonding in solids. In order to obtain U(7p) parameters, we carried out a DF average-of-configuration calculation for the neutral atom excited configuration $6p^67s^27p6d5f^2$ (the ground configuration is $6p^67s^26d5f^3$). The orbital energies (in eV) are -4.32 and -3.59 for $7p_{1/2}$ and $7p_{3/2}$, respectively, while the Slater exponents fitted to the DF charge density are 1.654 and 1.447 for the same AO's. The use of the 7p AO's instead of the 6p AO's still leads to linear UO_2^{2+} and UO_2 molecules, with the LUMO of UO_2^{2+} (or HOMO of UO_2) still 5u. However, the HOMO of UO_2^{2+} is now mostly O(2p), rather than mostly U($5f_{5/2}$, $m = \pm{}^1/_2$).

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(23) W. R. Wadt, private communication.

(24) D. W. Green, G. T. Reedy, and S. D. Gabelnick, *J. Nucl. Mater.*, **66**, 200 (1977).

(25) M. Kaufman, J. Muenter, and W. Klemperer, *J. Chem. Phys.*, **47**, 3365 (1967).

(26) G. V. Ionova and V. I. Spytsyn, *J. Phys.* (*Orsay, France*), **40**, C4-199 (1979).

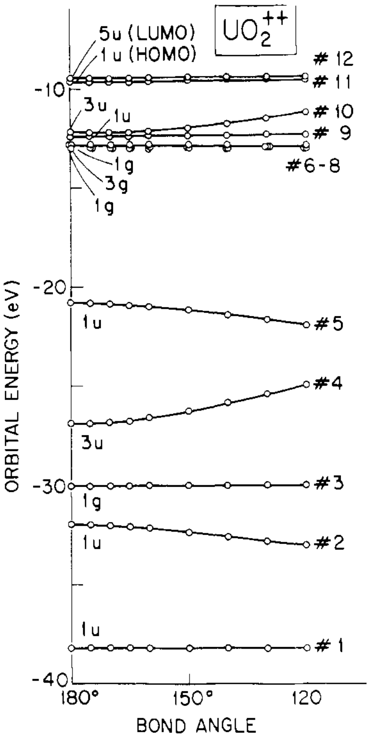

Figure 2. REX orbital energies vs. bond angle for UO_2^{2+}.

Table I. Mulliken Gross Atomic Populations for Uranium Compounds

molecule	7s	$6p_{1/2}$	$6p_{3/2}$	$6d_{3/2}$	$6d_{5/2}$	$5f_{5/2}$	$5f_{7/2}$
UO_2^{2+} [a]	0.01	1.90	3.52	0.09	0.11	1.08	0.70
UO_2^{2+} [b]	0.01	1.92	3.64	0.16	0.22	1.40	0.71
$UO_2Cl_4^{2-}$ [b]	0.00	1.93	3.63	0.31	0.42	1.47	0.70
UF_6 [c]	0.00	2.00	3.91	0.14	0.18	0.43	0.28
UF_6 [d]	−0.01	1.99	3.64	0.20	0.25	1.64	0.65
UCl_4	0.02	1.99	3.94	0.38	0.46	2.03	0.04
UCl_6	−0.04	2.00	3.95	0.29	0.39	0.52	0.24
$U(BH_4)_4$	−0.48	2.00	3.96	0.09	0.07	2.01	0.02
$U(COT)_2$	−0.59	2.00	4.00	0.06	−0.02	2.26	0.19

[a] Default O parameters. [b] Shifted O orbital energies. [c] Shifted F orbital energies, default F exponents. [d] Shifted F orbital energies, reduced F exponents.

Thus, we would agree with Tatsumi and Hoffmann[20] in that the 6p AO's do play an indirect role in making UO_2^{2+} linear because they push one (the σ_u) combination of the O(2p) AO's to high energies, thus making it possible for the HOMO (number 11) to be a mostly 5f MO.

Whereas complexes of UO_2^{2+} contain a linear array,[27] those of MoO_2^{2+} contain a bent MO_2^{2+} moiety.[28] Tatsumi and Hoffmann have recently considered the role of the linear 6p AO's of U in accounting for this difference.[20] We have computed REX orbital energies for MoO_2^{2+} as a function of the bond angle using the default parameters and assuming an Mo–O distance of 1.75 Å.[29] The minimum total orbital energy occurs at 111°, with a mostly O(2p) HOMO. The LUMO is mostly Mo(4d) and, when occupied, would appear to make the neutral molecule MoO_2 linear. We note that the $Mo^{IV}O_2$ moiety in $[MoO_2(CN)_4]^{4-}$ is linear,[30] with a Mo–O distance of 1.83 Å. However, the MoO_2 molecule is reported[31] from IR spectra in rare gas matrices to have a bond angle of 118 ● 4°.

The $UO_2Cl_4^{2-}$ orbital energies are also shown in Figure 1. For the sake of comparison, the same U–O distance as for uranyl (1.71 Å) was used. The U–Cl distance was 2.62 Å. The oxygen parameters are those of the parameter modifications section. Double-ζ orbital exponents[3] were used for Cl. The chlorine atoms introduce new levels coming from their 3s and 3p AO's. They also slightly perturb the uranyl levels. Such a ligand-induced decrease of the UO_2^{2+} "$6p_{3/2}$ splitting" from 7.0 to 5.5 eV due to a crystal field was discussed by Walch and Ellis.[17] We here find a decrease of the 3(1u)–1(3u) splitting from 6.1 eV for UO_2^{2+} to 5.1 eV for $UO_2Cl_4^{2-}$. In the present model, this decrease may be attributed to repulsion from the Cl(3s) 3u MO at 30.2 eV.

B. UF_6 and UCl_6. It is not surprising that almost all the existing relativistic molecular approaches have been tested on UF_6. These include the DS-DVM,[32-34] the DS-MSXα,[35] the quasi-relativistic MSXα or "RXα" approach,[36] and the pseudopotential approach.[37] The ionization energies obtained by these methods roughly agree with each other and with experiment.[35,36] The REX results in Figure 3 give for the t_{1u} HOMO a relativistic splitting of 1.5 eV, roughly agreeing with that found from ab initio calculations (1.1–1.3 eV[35]). This splitting is due to the mixing of the core 6p AO into this MO (3.5% $6p_{1/2}$ and 7.7% $6p_{3/2}$ in the γ_6^- and γ_8^- MO's, respectively). Thus it is clearly necessary to include the 6p's, and their relativistic splitting in order to describe the energy levels of UF_6. The rest of our fluorine 2p band is too low, but the order of the t_{1g}, t_{2u}, t_{1u}, and t_{2g} levels agrees with ref 37. The REX results differ from the ab initio ones by putting the a_{1g} MO lowest and the e_g in the middle of the 2p band. However, we clearly support the assignment made in ref 37 of the 1.2-eV separation of the first two peaks in the PES[38a] of UF_6 as arising from the γ_6^- and γ_8^- spin–orbit components of the t_{1u} HOMO.

The Mulliken populations are shown in Table I. Although UF_6 nominally is an $5f^0$ complex, we here find $6d^{0.44}5f^{2.2}$, in agreement with earlier calculations. The change of the F orbital exponents has a surprisingly large effect on this 5f character. Virtually all of it resides on the t_{1u} HOMO (11% and 48% of f character for γ_6^- and γ_8^-, respectively). The 6d character mainly comes from the t_{2g} MO.

The results for UCl_6 in Figure 3 again indicate a large relativistic splitting (1.1 eV) for the t_{1u} HOMO. Therefore, the nonrelativistic labels used for assigning the PES spectrum[38b] may not be satisfactory. Our other conclusions are rather uncertain. The spread of the 3p band is larger than the experimental one. Apart from the t_{1u} HOMO, and the e_g and a_{1g} MO's, our levels are in the order t_{1g}, t_{2u}, t_{1u}, and t_{2g}, as in the original assignment.[38b] The U hybridization, obtained here by using the unshifted double-ζ Cl, now is $6d^{0.69}5f^{0.76}$. Most of this f character again comes from the t_{1u} HOMO. Anyway, we conclude that both the 6d and the 5f AO's participate in the bonding of both UF_6 and UCl_6. The U–X overlap populations are positive, 0.10 and 0.070, while

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(27) For a tabulation of structures of UO_2^{2+} salts, see A. F. Wells, "Structural Inorganic Chemistry", 4th ed., Clarendon Press, Oxford, 1975, p 1000.

(28) For a review of Mo–O structures and bond lengths, see F. A. Schröder, *Acta Crystallogr., Sect. B*, **B31**, 2294 (1975).

(29) The distance in $MoO_2Br_2C_{10}N_2H_8$: R. H. Fenn, *J. Chem. Soc. A*, 1764 (1969).

(30) V. W. Day and J. L. Hoard, *J. Am. Chem. Soc.*, **90**, 3374 (1968).

(31) W. D. Hewett, Jr., J. H. Newton, and W. Weltner, Jr., *J. Phys. Chem.*, **79**, 2640 (1975).

(32) D. D. Koelling, D. E. Ellis, and R. J. Bartlett, *J. Chem. Phys.*, **65**, 3331 (1976).

(33) B.-I. Kim, H. Adachi and S. Imoto, *Chem. Lett. Jpn.*, 109 (1977).

(34) A. Rosén, *Chem. Phys. Lett.*, **55**, 311 (1978).

(35) D. A. Case and C. Y. Yang, *J. Chem. Phys.*, **72**, 3443 (1980).

(36) M. Boring and J. H. Wood, *J. Chem. Phys.*, **71**, 32 (1979).

(37) P. J. Hay, W. R. Wadt, L. R. Kahn, R. C. Raffenetti, and D. H. Phillips, *J. Chem. Phys.*, **71**, 1767 (1979).

(38) (a) UF_6: L. Karlsson, L. Mattsson, R. Jadrny, T. Bergmark, and K. Siegbahn, *Phys. Scr.*, **14**, 230 (1976); (b) UCl_6: G. Thornton, N. Edelstein, N. Rösch, R. G. Egdell, and D. R. Woodwark, *J. Chem. Phys.*, **70**, 5218 (1979).

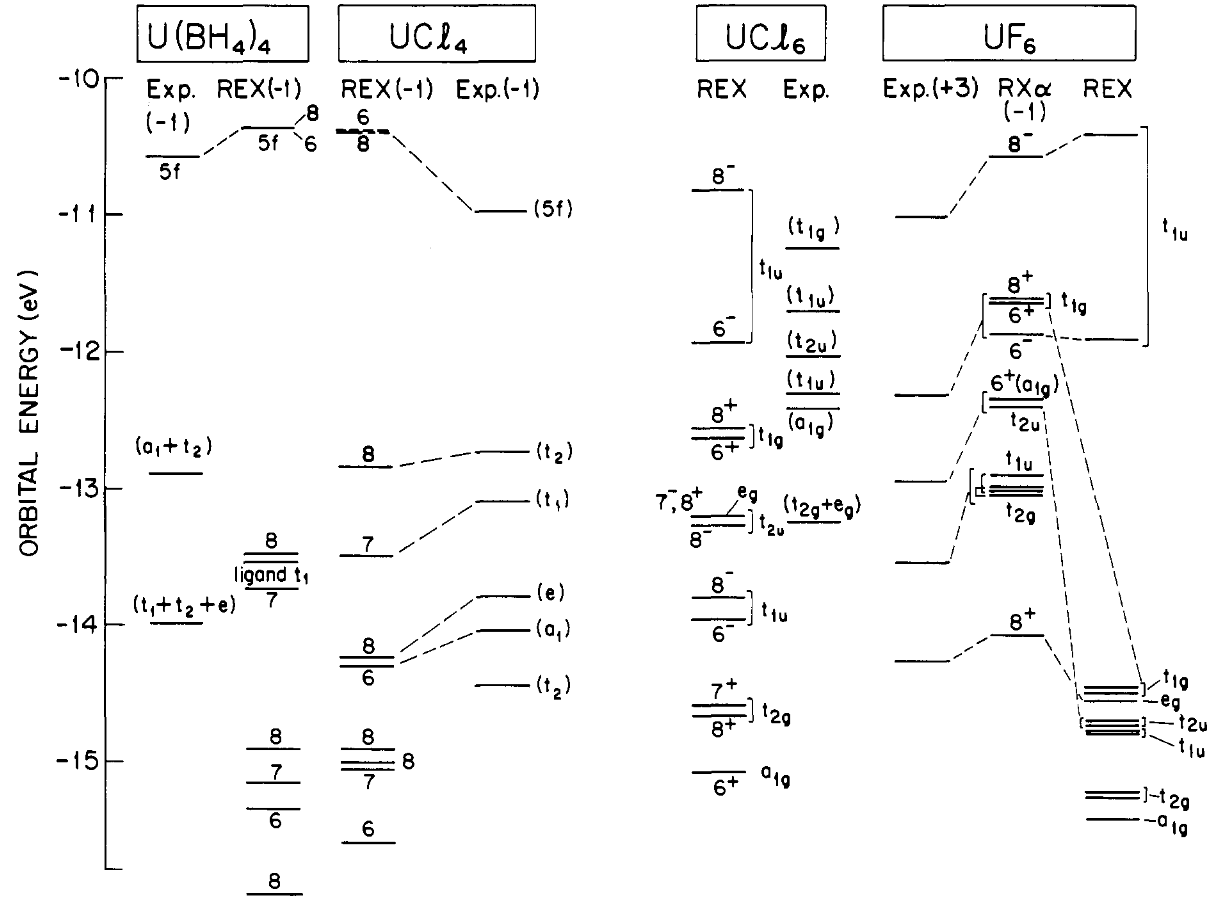

Figure 3. REX orbital energies for U(BH$_4$)$_4$, UCl$_4$, UCl$_6$, and UF$_6$ (with use of shifted F parameters and ζ for F$^-$). Columns headed "Exp." refer to PES data from ref 41b, 41a, 38b, and 38a, respectively. Values such as −1 in column headings denote shifts in electronvolts made for plotting convenience. Symmetry labels are those for the T_d* and O_h* groups.

the assumed[39a,b] U–X bond lengths were 1.994 and 2.42 Å for X = F and Cl, respectively.

C. UCl$_4$ and U(BH$_4$)$_4$. The orbital energies of these species are also shown in Figure 3. The U–Cl bond length was taken as 2.42 Å, to facilitate comparison with UCl$_6$. The experimental bond length[39c] is 2.53 Å. The BH$_4^-$ moieties were taken as tetrahedral with B–H = 1.30 Å. They are tridentately coordinated[40] to U with a U–B = 2.51 Å. The default parameters were used for B and H. In the f^2 species UCl$_4$, these two f electrons are now placed in a half-filled γ_8, which is almost degenerate with a γ_6. The most notable feature of the calculated UCl$_4$ spectrum is the relativistic splitting of the t$_2$ HOMO into a γ_7 and γ_8 by about 0.6 eV, analogously with the UCl$_6$ HOMO. The U–Cl overlap population is still positive and equal to 0.18 (UCl$_6$ had 0.07).

Orbital energies taken from the PES[41a] of UCl$_4$ are also shown in Figure 3. The experimental levels were assigned[41a] with the aid of nonrelativistic multiple scattering SCF-Xα calculations as arising from t$_1$(5f), t$_2$, t$_1$, e, a$_1$, t$_2$, and t$_2$(6p) MO's, respectively, in order of increasing binding energy. While the REX HOMO is also mostly 5f, the remaining REX MO's suggest a different assignment of the PES, namely, that the first two "ligand" PES bands, at 12.12 and 12.82 eV, respectively, correspond to the spin–orbit components γ_8 and γ_7 arising from t$_2$ and that the next two bands, at 13.07 and 13.47 eV, respectively, correspond to the γ_8 and γ_6 spin–orbit components arising from t$_1$. Some support for our assignment is given by the reported relative intensities, namely, that the ratios of the first band to the second band for these pairs are 2.1 and 1.7, respectively, close to the value of 2.0 expected for a γ_8,γ_7 or γ_8,γ_6 pair.

The PES[41b] of U(BH$_4$)$_4$ agrees with the REX results by putting a U(5f$_{5/2}$) level highest. Below the leads shown in Figure 3, REX gives γ_8, γ_7, and γ_6 levels at −18.63, −18.99, and −20.90 eV while the experimental values, with the same assignment, are at −17.78, −18.29, and −19.04 eV, respectively.[41b] Thus the theoretical 1t$_2$(γ_7 + γ_8) spin–orbit splitting is 0.36 eV and the experimental one 0.5 (1) eV. The γ_7 component has 0.7% U(6p$_{1/2}$) character while the γ_8 component has 3.9% U(6p$_{3/2}$) character. As the U atom 6p spin–orbit splitting is 9.76 eV, we indeed get about 4% of it. Otherwise this t$_2$ MO has about 40% of B(2s) character, the rest coming from the hydrogens. Analogously with UCl$_4$, the t$_2$(γ_7 + γ_8) at −12.754 and −12.496 eV again suffers a spin–orbit splitting of 0.26 eV. The γ_8 component has 1.9% 6p character.

In our model, U(BH$_4$)$_4$ is a highly ionic f^2 system. The total f population in Table I is 2.03. This actually agrees with our earlier conclusion[42] from a comparison of the experimental

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(39) (a) UF$_6$: D. Brown, "Halides of the Lanthanides and Actinides", Wiley, London, 1968, p 25; (b) UCl$_6$: W. Zachariasen, *Acta Crystallogr.*, **1**, 285 (1948); (c) UCl$_4$: Yu. S. Ezhov, P. A. Akishin, and N. G. Rambidi, *Zh. Strukt. Khim.*, **10**, 763 (1969); *J. Struct. Chem.*, **10**, 661 (1969).

(40) The bond lengths are those of solid U(BH$_4$)$_4$ as given by E. R. Bernstein, W. C. Hamilton, T. A. Keiderling, S. J. LaPlaca, S. J. Lippard, and J. J. Mayerle, *Inorg. Chem.*, **11**, 3009 (1972), while the assumed shape is an idealization of that of gaseous Zr(BH$_4$)$_4$ as given by V. Plato and K. Hedberg, *ibid.*, **10**, 590 (1971).

(41) (a) UCl$_4$: J. M. Dyke, N. K. Fayad, A. Morris, I. R. Trickle, and G. C. Allen, *J. Chem. Phys.*, **72**, 3822 (1980); (b) U(BH$_4$)$_4$: A. J. Downs, R. G. Egdell, A. F. Orchard, and P. D. P. Thomas, *J. Chem. Soc., Dalton Trans.*, **1755** (1978).

(42) See Table 15 in P. Pyykkö and J. P. Desclaux, *Chem. Phys.*, **34**, 261 (1978).

U–X bond lengths with those calculated for the model system UH_6 with and without 5f AO's. While the halides UX_6 had a Δ(X–H) bond length difference, indicating 5f contributions to bonding, the U–H_b of $U(BH_4)_4$ did not.[42]

D. $U(COT)_2$. As the question of the role of 5f AO's in the bonding in $U(COT)_2$, where COT denotes cyclooctatetraene, is of considerable interest,[43] we have carried out a REX calculation assuming an idealized D_{8h} geometry. We used the observed[44,45] U–C and C–C bond distances of 2.65 and 1.39 Å, respectively, together with an assumed C–H distance of 1.0 Å, and default parameters for all atoms. The U basis set consisted of 7s, 6p, 6d, and 5f AO's, as in the case of UO_2^{2+}, so that the number of spin orbitals considered was 192. The computed atomic charges and overlap populations are as follows: U, +4.10; C, –0.31; H, +0.05; U–C, –0.169; C–C, +1.133; C–H, +0.962; U–H, –0.024. Thus the REX description of the bonding is essentially ionic, characterized by a charge of approximately +4 for U. This result is almost a trivial consequence of our model, as the overlap interactions are small at the U–C distance of 2.65 Å. The total populations in the $5f_{5/2}$ and $5f_{7/2}$ orbitals are 2.26 and 0.19, respectively. The "frontier" orbitals for $U(COT)_2$ are, in D_{8h}^* notation, a $5u(e_{5/2u})$ orbital at –9.42 eV, which is 95.8% $5f_{5/2}$, $|m| = {}^5/_2$, and a $1u(e_{1/2u})$ orbital at –9.41 eV which is 99.6% $5f_{5/2}$, $|m| = {}^1/_2$. Assigning one electron to each of these nearly degenerate Kramers doublets yields total states with $|M| = 2$ and 3, the latter presumably being the ground state. Thus the REX description of the electronic structure is related to that given by Hayes and Edelstein,[46] who carried out a Wolfsberg–Helmholz calculation using only U(5f) and C($2p_\pi$) AO's, with overlap integrals obtained using U^{4+} Dirac–Fock radial functions. They also carried out a two-electron ligand field calculation with spin–orbit coupling, yielding a ground state with $|m| = 3$ and with a magnetic moment in essential agreement with experiment.[47] More recently Rösch and Streitwieser[48] have carried out SCF-Xα–scattered-wave MO calculations on $Th(COT)_2$ and $U(COT)_2$ and have compared their results to the photoelectron spectra of Clark and Green.[49,50] The agreement is reasonably satisfactory, especially as the calculations did not include relativistic effects.

In Figure 4 we compare the REX orbital energies (shifted upward by 3 eV) and the observed[49,50] vertical ionization energies, the latter labeled by the assignments of Rösch and Streitwieser.[48] The highest occupied REX MO's, excluding the mostly 5f 1u and 5u MO's, are a 3u,5u pair corresponding to a nonrelativistic e_{2u} MO and a 3g,5g pair corresponding to a nonrelativistic e_{2g} MO. The computed spin–orbit splittings of these pairs are only 0.04 and 0.02 eV, respectively, too small to be shown in Figure 3 and much smaller than the analogous splittings of the highest mostly ligand MO's of UF_6, UCl_6, and UCl_4. The central atom AO fractions in these MO's are as follows: 3g, 8.7% $d_{3/2}$, 2.1% $d_{5/2}$; 5g, 10.5% $d_{5/2}$; 3u, 12.9% $f_{5/2}$, 1.6% $f_{7/2}$; 5u, 3.2% $f_{5/2}$, 5.4% $f_{7/2}$. The $6p_{3/2}$ fraction in the 3u MO is negligible since the 3u,5u pair derives from e_{2u}, while the p AO's derive from $a_{2u} + e_{1u}$ when spin is conserved. This accounts for the small spin–orbit splitting discussed above. The large number (28) of ligand MO's with shifted energies between –8 and –15 eV makes further assignments difficult.

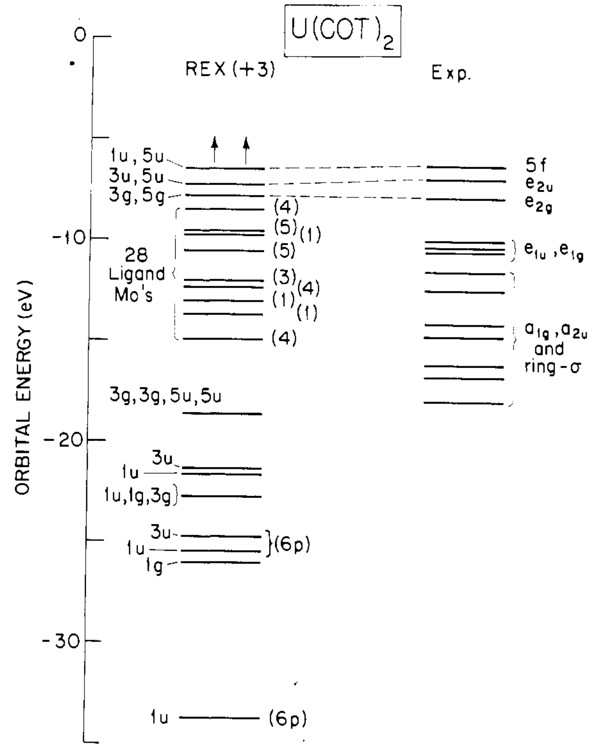

Figure 4. REX orbital energies (shifted upward by 3 eV) for $U(COT)_2$ compared to the PES data from ref 49 and 50 as assigned in ref 48. Numbers to the right of the REX values lying between –8 and –15 eV denote the number of nearly degenerate levels.

E. Splittings of U(5f) Energy Levels. In Figure 5 we present the energies of the mostly 5f MO's for UO_2^{2+} (shifted O parameters and double-ζ Cl AO's), UCl_6 (double-ζ Cl AO's), UF_6 (shifted F parameters with ζ for F^0 and with ζ for F^-), and $U(COT)_2$. For comparison the U atomic 5f levels are shown at the right. Not shown are the levels for UCl_4 and $U(BH_4)_4$ for which the "crystal field" splittings of the atomic 5f levels are computed to be 0.01 eV or less. The levels of $U(COT)_2$ are not much perturbed, the separation between 1u and lowest level 5u being only 0.006 eV, while 3u is 0.14 above 1u. These separations are within the $f_{5/2}$ manifold; those within $f_{7/2}$ are 0.06 eV or less.

The REX descriptions of UO_2^{2+} and $UO_2Cl_4^{2-}$, as described in the section A of the U compounds, involve a filled mostly 5f 1u MO. The other 5f levels lie higher by 0.24 (5u), 0.33 (3u), 0.98 (5u, 7u), 1.10 (1u), and 1.40 (3u) eV. By comparison, the Dirac–Slater optical transition-state values of Walch and Ellis[17] are 0.54 (5u), 0.68 (3u), 1.50 (5u, 7u), and 3.95 (1u); they do not report a value for the upper 3u MO. Their virtual energies are closer to ours, namely, 0.27 (5u), 0.41 (3u), 1.22 (5u, 7u), and 3.81 (1u). The changes in the REX values in going to $UO_2Cl_4^{2-}$ are rather modest.

The UCl_6 REX energies relative to the lower 7^- component are 0.24 (8^-), 0.75 (7^-), 0.94 (8^-), and 1.00 (6^-) eV. The symmetry labels are abbreviated as $6^- = \gamma_6^- = \gamma_{6u}$, $7^- = \gamma_7^- = \gamma_{7u}$, and $8^- = \gamma_8^- = \gamma_{8u}$. Experimental[51] excitation energies for UCl_6^- in $(Et_4N)UCl_6$ are 0.84 (7^-), 1.26 (8^-), and 1.42 eV (6^-); the energy of the lower 8^- component was not reported. A recent quasi-relativistic SCF-Xα study[52] yielded excitation energies for UCl_6^- of 0.28 eV for t_{2u} ($7^- + 8^-$) and 1.05 eV for t_{1u} ($6^- + 8^-$), both relative to the a_{2u} (7^-) lowest energy component. The corresponding weighted averages of REX energies are 0.41 eV for t_{2u} and 0.96 eV for t_{1u}. Thus, the REX

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(43) For reviews of structure and bonding in $U(COT)_2$ see: (a) E. C. Baker, G. W. Halstead, and K. N. Raymond, *Struct. Bonding (Berlin)*, **25**, 23 (1976); (b) T. J. Marks, *Prog. Inorg. Chem.*, **25**, 223 (1979).

(44) A. Zalkin and K. N. Raymond, *J. Am. Chem. Soc.*, **91**, 5667 (1969).

(45) A. Avdeef, K. N. Raymond, K. O. Hodgson, and A. Zalkin, *Inorg. Chem.*, **11**, 1083 (1972).

(46) R. G. Hayes and N. Edelstein, *J. Am. Chem. Soc.*, **94**, 8688 (1972).

(47) D. G. Karraker, J. A. Stone, E. R. Jones, Jr., and N. Edelstein, *J. Am. Chem. Soc.*, **92**, 4841 (1970).

(48) N. Rösch and A. Streitwieser, *J. Organomet. Chem.*, **145**, 195 (1978).

(49) J. P. Clark and J. C. Green, *J. Organomet. Chem.*, **112**, C14 (1976).

(50) J. P. Clark and J. C. Green, *J. Chem. Soc., Dalton Trans.*, 505 (1977).

(51) J. L. Ryan, *J. Inorg. Nucl. Chem.*, **33**, 153 (1971).

(52) G. Thornton, N. Rösch, and N. Edelstein, *Inorg. Chem.*, **19**, 1304 (1980).

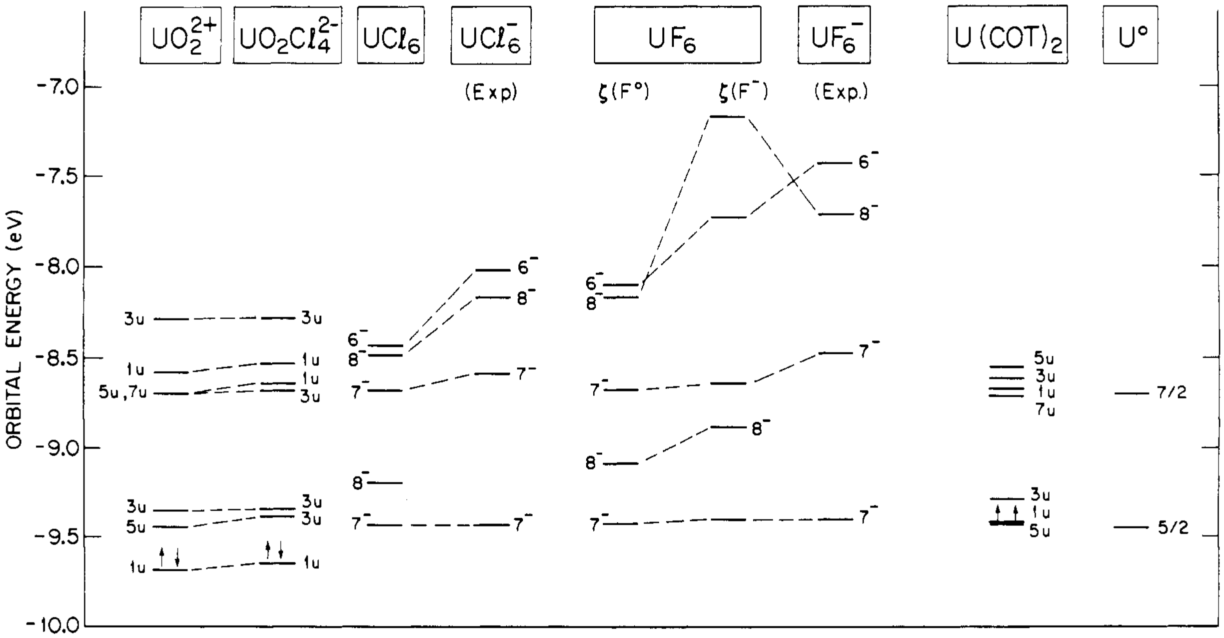

Figure 5. REX energies for the mostly U(5f) MO's of UO_2^{2+}, $UO_2Cl_4^{2-}$, UCl_6, UF_6 (both with F^0 and F^- ζ values), and $U(COT)_2$. Columns headed "Exp." refer to spectral data on UX_6^- salts from ref 51.

excitation energies obtained with use of the UCl_6 bond length of 2.42 Å are 70–90% of the observed UCl_6^- values and 90% of the SCF-Xα value for the t_{1u} ($6^- + 8^-$) component.

Similar results obtained for UF_6, with REX energies relative to the lower 7^- component of 0.33 (8^-), 0.74 (7^-), 1.25 (8^-), and 1.32 (6^-) eV. Experimental[51] excitation energies for UF_6^- in $(Ph_4As)UF_6$ are 0.92 (7^-), 1.70 (8^-), and 1.97 eV (6^-). The use of $\zeta(F^-)$ instead of $\zeta(F^0)$ raises the REX values to 0.51 (8^-), 0.75 (7^-), 2.23 (8^-), and 1.68 eV (6^-); note the inversion of the two highest components. The recent relativistic effective core potential calculations[37] of Hay et al. in which spin–orbit coupling is treated as a perturbation yield excitation energies for UF_6^- (relative to 7^-) of 0.67 (8^-), 0.97 (7^-), 1.80 (8^-), and 1.95 eV (6^-). Thus, the use of $\zeta(F^-)$ instead of $\zeta(F^0)$ gives a spread of REX eigenvalues in better agreement with observed and calculated UF_6^- excitation energies, although the order of the 6^- and the upper 8^- level is inverted. It should be noted that 6^- and 8^- levels also arise from the ligand $p_\sigma(t_{1u})$ orbitals of a MX_6 complex, whereas 7^- can only arise from the ligand $p_\pi(t_{2u})$ orbitals, so that the energies of the 6^- and 8^- levels are more sensitive than that of the 7^- levels to changes in the REX parameterization.

Other Heavy Element Compounds

A. Lanthanoid Triiodides. The calculated bond angles for LaI_3, GdI_3, and LuI_3 are shown in Table II. A "high-spin" f^7 configuration for Gd(III) was imposed by assuming half-filled MO's in calculating the total orbital energy for GdI_3. As seen, LaI_3 is predicted to have the smallest β; the angle opens up with the increasing Z while the d character decreases. This trend was also observed in a self-consistent charge extended Hückel study,[53] which omitted f orbitals and electrons, of the trihalides of La, Ce, Eu, Gd, Er, and Lu. The experimental bond angles for GdI_3 and LuI_3 are slightly larger than our calculated ones but still correspond to nonplanar and hence polar molecules. The corresponding trifluorides have been reported[54] to be polar as well. The assumption of planarity made by Bender and Davidson in their recent semiempirical study[55] of 56 LnX_3 molecules (Ln = Ce → Lu; X = F → I) thus appears to have been unwarranted. As seen from Table III, the $h_{ii}(5d)$ goes up with increasing Z. This trend is due to the relativistic SCF expansion and to an "SCF lanthanoid expansion" of the 5d's. The latter effect has been recently discussed.[56] At the same time $h_{ii}(6s)$ goes down, both because of the lanthanoid contraction and relativity.

Table II. Bond Angles β (Deg) for LaI_3, GdI_3, and LuI_3

	β^a				
molecule	REX	exptl	R,[a] Å	$Q(5d)^b$	$Q(6s)^b$
$LaI_3{}^c$	100		2.946^f	1.00	0.12
$LaI_3{}^d$	106		2.946^f	0.85	0.10
$GdI_3{}^{c,e}$	102	108.0 (2.0)[g]	2.841^g	0.82	0.17
$LuI_3{}^c$	106	114.5 (2.1)[g]	2.771^g	0.60	0.23

[a] β is the I-M-I angle, R the M-I bond length. [b] Mulliken gross atomic populations. [c] With 5p AO's. [d] With 6p AO's. [e] The f^7 configuration is obtained by using half-filled MO's for them. [f] Predicted value from K. S. Krasnov, N. I. Giricheva, and G. V. Girichev, *J. Struct. Chem.* (*Engl. Transl.*), 17, 575 (1976). [g] N. I. Popenko, E. Z. Zasorin, V. P. Spiridonov, and A. A. Ivanov, *Inorg. Chim. Acta,* 31, L371 (1978).

B. PoH_2 and (eka)PoH_2. REX and EHT calculations on PoH_2 with the assumptions of equal relativistic and nonrelativistic bond lengths of 1.75 Å yield minimum total orbital energies for bond angles β of 95.1 and 98.1°, respectively. The relativistic decrease in β arises from the 4.1-eV stabilization of the Po(6s) AO. The computed angle is undoubtedly too large, as the observed value[57] for TeH_2 is 90.2°, while REX calculations yield 99.6° with a relativistic decrease of 1.3°. A smaller β value, 92.5°, is computed for (eka)PoH_2 (Z = 116), for which $\alpha(7s) = -27.2$ eV, 5.1 eV below the relativistic value of $\alpha(6s)$ for Po and 9.2 eV below the nonrelativistic value of $\alpha(6s)$ for Po. The basis set for (eka)Po consisted of 7s, 7p, and 6d AO's, while those for Po consisted of 6s and 6p AO's only.

Figure 6 displays the energies for the highest three occupied MO's of PoH_2 as a function of β. Not shown is the low energy

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(53) C. E. Myers, L. J. Norman, II, and L. M. Loew, *Inorg. Chem.*, **17**, 1581 (1978).

(54) E. W. Kaiser, W. E. Falconer, and W. Klemperer, *J. Chem. Phys.*, **56**, 5392 (1972).

(55) C. F. Bender and E. R. Davidson, *J. Inorg. Nucl. Chem.*, **42**, 721 (1980).

(56) P. Pyykkö, *Phys. Scr.*, **20**, 647 (1979).

(57) G. Herzberg, "Electronic Spectra of Polyatomic Molecules", Van Nostrand, Princeton, NJ, 1966, p 587.

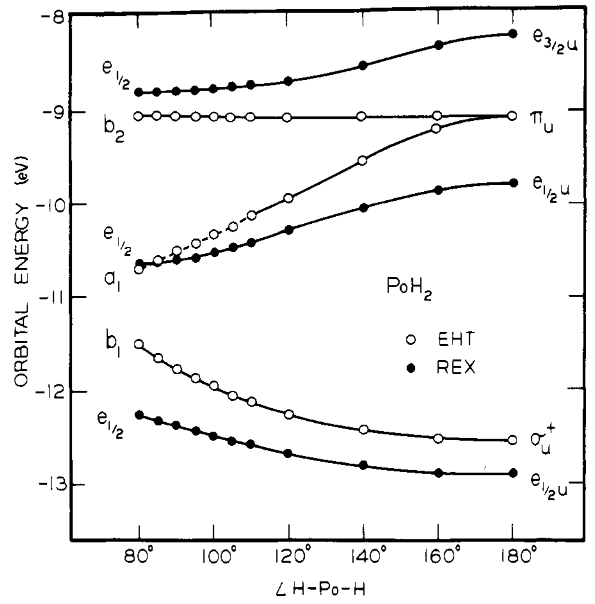

Figure 6. REX (solid circles) and EHT (open circles) orbital energies vs. bond angle β for PoH_2. Curves are labeled by symmetry designations for the groups C_{2v}* and $D_{\infty h}$* (REX), and C_{2v} and $D_{\infty h}$ (EHT).

mostly 6s MO. There is only one irreducible representation, $e_{1/2}$, for the double group C_{2v}*, so all REX MO's have the same designation except at $\beta = 180°$. We note that the spin-orbit splitting (REX points) of 1.6 eV for the π_u level into $e_{3/2u}$ and $e_{1/2u}$ components at $\beta = 180°$ is comparable to the nonrelativistic splitting (EHT points) of 1.4 eV of π_u into b_2 and a_1 components at $\beta = 90°$, so that the separation of the two highest occupied REX MO's is essentially constant over the entire range of β.

The REX program permits a population analysis to be made in an atomic $|lsjm\rangle$ basis rather than the customary real orbital basis. The former basis is used both with the REX and EHT parameterizations. Thus we can follow the tendency for the $np_{1/2}$ orbitals to become "isolated" as a consequence of their relativistic stabilization relative to $np_{3/2}$. For (eka)PoH_2, where the atomic splitting is 8.0 eV (Table III), the isolation is striking, with an MO that is approximately 86% $7p_{1/2}$ at the low energy of −15.3 eV. For PoH_2, where the atomic splitting is 2.8 eV, the isolation is less striking but still apparent, with the corresponding MO having approximately 58% $6p_{1/2}$ character and an energy of −12.4 eV. With the EHT parameterization, there is no MO with a dominantly $6p_{1/2}$ character. The ratio of Mulliken gross atomic populations (summed over m_j components and over occupied MO's) for $6p_{3/2}$ and $6p_{1/2}$ is 1.68 with use of REX parameters for PoH_2 at $\beta = 95°$, while it is 1.82 at $\beta = 180°$. Both values are below that of 2.0 which obtains for all β with EHT parameters, indicating a tendency to minimize $6p_{3/2}$ occupancy in the relativistic case. Another measure of the effect of relativity is given by the composition of the HOMO, which with the EHT parameterization is a nonbonding b_2 MO consisting purely of $6p_\pi$, corresponding to $^1/_3 6p_{1/2}$ and $^2/_3 6p_{3/2}$ in character. With the REX parameterization, the HOMO is a slightly antibonding $e_{1/2}$ MO with a composition of 3.5% from each H(1s), 11% Po($6p_{1/2}$), and 82% Po($6p_{3/2}$), reflecting the tendency toward $6p_{1/2}$ concentration in a lower energy MO.

Following the type of analysis given by Pitzer[8a] for the bonding in TlH, we now examine the bonding in PoH_2 in the limit of complete isolation in the core of the Po 6s and $6p_{1/2}$ electrons. Assuming a 90° bond angle, with H atoms on the x and y axes of a Cartesian axis system with the Po atom at the center, a nonrelativistic description would involve simple valence bonds between H(1s) and Po($6p_\sigma$) AO's with an

Table III. REX Parameters

element	orbital[a]	$-\alpha_i$, eV	ζ_i
H	1s	13.61, 10.00	1.00
B	2s	13.47	1.265
	2p	8.43	1.134
C	2s	19.39	1.577
	2p	11.07	1.435
O	2s	34.08, 30.08[b]	2.194
	2p*	16.78, 12.78[b]	2.020
	2p	16.74, 12.74[b]	2.017
F	2s	42.88, 37.90[b]	2.501
	2p*	19.90, 14.90[b]	2.308
	2p	19.83, 14.83[b]	2.303
F^-	2s	37.90[b]	2.386[c]
	2p*	14.90[b]	1.972[c]
	2p	14.83[b]	1.965[c]
Cl	3s	29.38	2.267
	3p*	13.86	2.067 10 (0.919 490),[d] 0.773 385 (0.149 084)[d]
	3p	13.72	2.058 43 (0.918 358),[d] 0.776 501 (0.149 436)[d]
I (nonrel)[f]	5s	22.34	2.626
	5p	10.97	2.198
I (rel)	5s	23.86	2.731
	5p*	11.72	2.289
	5p	10.58	2.186
La	6s	4.89	1.377
	6p*	3.32[e]	1.184[e]
	6p	3.18[e]	1.137[e]
	5d*	6.48	1.920
	5d	6.35	1.889
Gd	6s	5.44	1.520
	5p*	37.34	3.636
	5p	32.70	3.429
	5d*	6.14	2.056
	5d	5.97	2.009
	4f*	20.11	5.429
	4f	19.35	5.364
Lu	6s	6.06	1.666
	5p*	44.24	4.124
	5p	36.95	3.810
	5d*	5.21	2.041
	5d	5.04	1.979
	4f*	23.27	6.482
	4f	21.52	6.355
Po (nonrel)[b]	6s	17.97	2.720
	6p	9.05	2.245
Po (rel)	6s	22.04	3.067
	6p*	10.98	2.538
	6p	8.22	2.221
At (nonrel)[f]	6s	20.83	2.870
	6p	10.34	2.405
At (rel)	6s	25.53	3.229
	6p*	12.80	2.724
	6p	9.33	2.369
Rn (nonrel)[f]	6s	23.78	3.014
	6p	11.65	2.556
Rn (rel)	6s	29.16	3.384
	6p*	14.70	2.900
	6p	10.45	2.517
U	7s	5.51	1.728
	6p*	36.55	3.907
	6p	26.80	3.425
	6d*	5.24	2.062
	6d	4.99	1.975
	5f*	9.44	3.866
	5f	8.70	3.761
(eka)Po	7s	27.16	3.754
	7p*	14.67	3.216
	7p	6.69	2.242
	6d*	36.80	4.788
	6d	30.97	4.497

[a] nl* denotes $j = l - {}^1/_2$, nl denotes $j = l + {}^1/_2$. [b] Shifted values; see section on parameter modifications. [c] Based on F^- values of F; see section on parameter modifications. [d] Double-ζ exponents followed by coefficients in parentheses. [e] Obtained from 6s6p5d excited-state Dirac–Fock calculation. [f] nonrel = nonrelativistic; rel = relativistic.

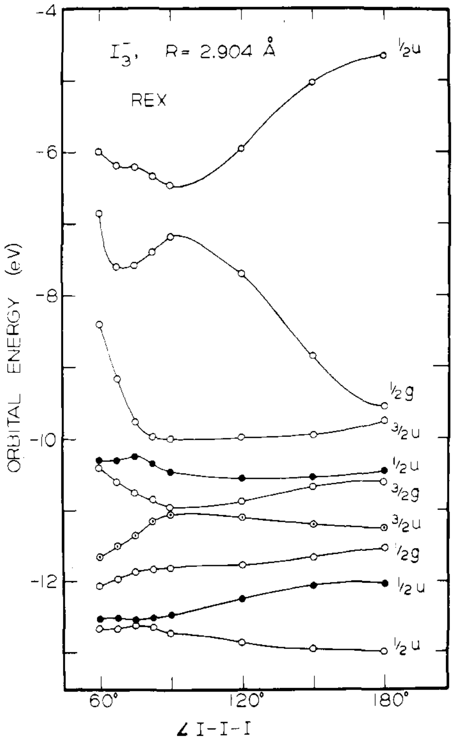

Figure 7. REX orbital energies vs. bond angle for I_3^-, with a bond length of 2.904 Å.

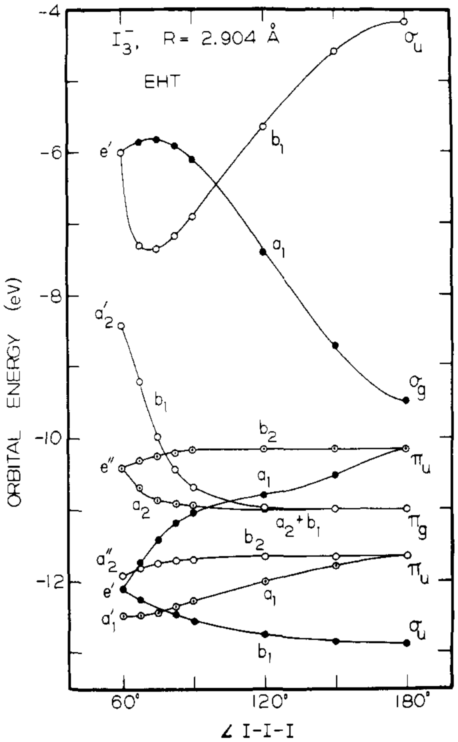

Figure 8. EHT orbital energies vs. bond angle for I_3^-, with a bond length of 2.904 Å.

overlap integral S. However, inspection of the form of p AO's in a $|lsjm\rangle$ quantization shows in the strongly relativistic limit of $6p_{1/2}$ isolation that the square of the overlap between a H(1s) AO on the x axis and a $p_{3/2(\pm3/2)}$ orbital would be $S^2/2$, while that to a $p_{3/2(\pm1/2)}$ orbital would be $S^2/6$. The remaining one-third σ-bonding capability is "tied-up" in the $p_{1/2}$ AO's and thus is not available. The expectation is then for a relativistic weakening of bond strength, although less extreme than is the case for TlH with its "$p_{1/2}$ bond".[58]

C. Polyhalide Anions I_3^- and AtI_2^-. REX and EHT orbital energies as a function of bond angle for I_3^- with use of the observed I–I distance[59] of 2.904 Å are shown in Figures 7 and 8, respectively. The corresponding total orbital energies vs. bond angle indicate the following trends: (a) a bond angle of 180° as observed[59] (REX and EHT); (b) a bond angle of approximately 103° for I_3^+ (REX and EHT), close to the values of 97° estimated[60] from ^{127}I NQR for $I_3^+\ AlCl_4^-$ and 96.7° measured[61] for the related $ICl_2^+AlCl_4^-$; (c) the REX energy of atomization for I_3^- (0.4 eV) is less than the EHT value (0.5 eV), indicating a relativistic weakening of the bonds; (d) by contrast, the REX energy of atomization for I_3^+ (4.0 eV) is greater than the EHT value (2.4 eV); (e) the HOMO for collinear I_3^- is of symmetry $^1/_2g$ (REX) or σ_g^+ (EHT), with a composition that is largely $5p_{3/2}$ ($m = \pm^1/_2$) from the terminal I atoms; the energy of this MO rises steeply as the bond angle is reduced (Figures 7 and 8).

The EHT orbital energies in Figure 6 for the 180° bond angle are in the same order as those computed[62] by Datta et al. using an ab initio effective potential method involving a positive counterion shell which lowered all MO energies by a nearly constant value of 3.3 ± 0.2 eV.

The unstable element astatine is commonly studied[63] in an iodine carrier such as AtO_3^- in IO_3^- or AtI_2^- in I_3^-. As a complement to our study of I_3^-, we have made calculations for collinear AtI_2^-, both with $D_{\infty h}$ (central At) and $C_{\infty v}$ (terminal At) symmetries. With the assumption of the same bond length of 2.904 Å for both I–I and At–I bonds are used for I_3^-, the $D_{\infty h}$ structure is more stable than the $C_{\infty v}$ structure by 1.0 eV (REX). However, the nonrelativistic stabilization is only 0.2 eV (EHT). The $D_{\infty h}$ structure is characterized by computed REX charges of +0.30 (At) and −0.65 (I), in contrast to charges of +0.14 and −0.57 in I_3^- for the central and terminal atoms, respectively, reflecting the fact that the At($6p_{3/2}$) orbital energy is 1.2 eV higher than that for I($5p_{3/2}$) (Table III). Although in our one-electron description AtI_2^- is *higher* in energy than $At^+ + 2I^-$ by 0.8 (REX) or 0.7 eV (EHT), the energies of atomization (to form $I + I^- + At$) are 0.4 (REX) and −0.02 eV (EHT) for the $D_{\infty h}$ structure, the former equaling the corresponding I_3^- values. Thus again a relativistic enhancement of molecular stability is indicated. The difference between At and I is most easily illustrated by their diatomic hydrides. The dissociation energy of HAt is being measured[64] and is according to the preliminary results considerably smaller than that of HI, namely, 2.3–2.7 eV for HAt vs. 3.06 eV for HI.[65] We compute 3.7 eV for HAt with R = 1.70 Å vs. 4.4 eV for HI with R = 1.61 Å; the corresponding EHT values are 5.0 eV for both molecules, illustrating a greater relativistic reduction in bond strength for HAt as compared to HI.

D. Radon Difluoride. The molecule RnF_2 displays a relativistic *enhancement* of bond strength, with the computed energies of atomization being 18.1 (REX) and 16.0 eV (EHT) at an assumed bond length of 2.5 Å. In our one-electron

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(58) P. Pyykkö and J. P. Desclaux, *Chem. Phys. Lett.*, **42**, 545 (1976).

(59) E. E. Havinga and E. H. Wiebenga, *Acta Crystallogr.*, **11**, 733 (1958).

(60) D. J. Merryman, J. D. Corbett, and P. A. Edwards, *Inorg. Chem.*, **14**, 428 (1975). The ion Te_3^{2-}, isoelectronic with I_3^+, is also bent, with an angle of 113.1° [A. Cisar and J. D. Corbett, *Inorg. Chem.*, **16**, 632 (1977)].

(61) G. G. Vonk and E. H. Wiebenga, *Acta Crystallogr.*, **12**, 859 (1959).

(62) S. N. Datta, C. S. Ewig, and J. R. Van Wazer, *J. Mol. Struct.*, **48**, 407 (1978).

(63) For reviews of astatine chemistry, see: (a) A. H. W. Aten, Jr., *Adv. Inorg. Chem. Radiochem.*, **6**, 207 (1964); (b) E. H. Appelman, *MTP Int. Rev. Sci.: Inorg. Chem., Ser. One*, **3**, 187–198 (1972); W. A. Chalkin, E. Herrmann, J. W. Norseev, and I. Dreyer, *Chem. Ztg.*, **101**, 470 (1977).

(64) J. R. Grover, D. E. Malloy, and J. B. A. Mitchell, Abstracts, 7th International Symposium of Molecular Beams, Riva del Garda, Italy, May 1979, pp 90–92 (unpublished).

(65) B. Rosen, "Données Spectroscopiques Relatives aux Molécules Diatomiques", Pergamon Press, Oxford, 1970, p 188.

description using the default parameters, the molecule is essentially ionic (Rn^{2+}, $2F^-$) so that the difference of 2.1 eV in these two energies is approximately twice the 1.2 eV atomic spin–orbit destabilization of $6p_{3/2}$ from −11.6 eV (EHT) to −10.4 eV (REX).

Summary

Comparisons of REX orbital energies to those calculated by other theoretical methods and to those obtained from PES data indicate the usefulness of the REX method for obtaining semiquantitative estimates of spin–orbit splittings of valence molecular orbitals in compounds of uranium. The "crystal-field" splittings of the 5f levels in these compounds are also adequately accounted for by the REX method. There are some particularly interesting features of the REX descriptions of uranium compounds: the occurrence of a mostly 5f MO as the HOMO in UO_2^{2+}; spin–orbit splittings of at least 1 eV for the t_{1u} HOMO's of UF_6 and UCl_6; essentially ionic descriptions of the bonding in $U(BH_4)_4$ and $U(COT)_2$; nearly degenerate $|m| = {}^1/_2$ and ${}^5/_2$ mostly $5f_{5/2}$ levels as HOMO's in $U(COT)_2$, so that a "high-spin" $|M| = 3$ ground state is expected, in accord with earlier ligand field calculations.[46]

Comparative studies for some compounds of Po, At, and Rn with the use of the relativistic (REX) and nonrelativistic (EHT) parameterizations suggest a number of relativistic trends in bonding. The REX description of PoH_2, and to a greater extent that of (eka)PoH_2, is characterized by a tendency toward $p_{1/2}$ rather than p_σ bonding. A substantial relativistic stabilization of the $D_{\infty h}$ structure of collinear AtI_2^- relative to the $C_{\infty v}$ structure is predicted. In contrast to results for compounds of Tl or Pb, the REX description of RnF_2 involves a relativistic enhancement of bond strength arising from the spin–orbit destabilization of the $6p_{3/2}$ orbitals. These and other results obtained by our method[1,3] indicated its usefulness in establishing guidelines as to the significance of relativistic effects in chemistry.

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Appendix

The atomic orbital energies α_i and the Slater exponents ζ_i used in this study are listed in Table III. For Cl(3p) our double-ζ functions[3] were used. See the parameterization section for discussion of the parameters and their modifications.

Registry No. UO_2^{2+}, 16637-16-4; $UO_2Cl_4^{2-}$, 19160-32-8; UF_6, 7783-81-5; UCl_4, 10026-10-5; UCl_6, 13763-23-0; $U(BH_4)_4$, 12523-77-2; $U(COT)_2$, 11079-26-8; LaI_3, 13813-22-4; GdI_3, 13450-91-4; LaI_3, 13813-45-1; PoH_2, 31060-73-8; I_3^-, 14900-04-0; AtI_2^-, 77189-82-3; RnF_2, 18976-85-7.

Supplementary Material Available: A listing of the relativistic and nonrelativistic atomic orbital energies and Slater exponents for all elements (3 pages). Ordering information is given on any current masthead page.

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Use of the Jahn–Teller Theorem in Inorganic Chemistry

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The observed distortions from octahedral geometry in Cu^{II} complexes of local stoichiometry MY_6 and *trans*-$MY_4Y'_2$ are well described in qualitative terms by (a) s–d mixing and (b) the relative stabilization energies of square-planar MY_4 and $MY_2Y'_2$ units via the angular-overlap model. No recourse is made to the enigmatic symmetry results of the first- and second-order Jahn–Teller approaches within the d-orbital manifold.

Introduction

Many structural and dynamic aspects of transition-metal chemistry are currently rationalized with use of the Jahn–Teller theorem,[2] which asserts that a molecule in an orbitally degenerate electronic state will distort to remove the degeneracy. Present usage of the theorem[3] in this area may be summarized by two comments. (a) In most point groups, asymmetric occupation of degenerate orbitals leads to a degenerate electronic state. An exception occurs in groups such as D_{4h} and D_{8h} where no degenerate state is so produced. The classic case of singlet cyclobutadiene[4] is an example of this type. (b) Substituted octahedral compounds (for example, *cis*-$MY_4Y'_2$, where the point symmetry is low and degenerate representations do not occur, are structurally very similar to their totally substituted parent (MY_6), where a degenerate electronic state is possible at the undistorted geometry.

Where the first-order Jahn–Teller theorem (applicable to degenerate electronic states only) may not be used, higher order variants[5] often allow rationalization of the structural results. Equation 1 shows a perturbation theoretic expansion

$$E(0) = \langle 0|\mathcal{H}_q|0\rangle q + \frac{1}{2}\left[\langle 0|\mathcal{H}_{qq}|0\rangle - 2\sum_n{}' \frac{|\langle 0|\mathcal{H}_q|n\rangle|^2}{\Delta E_{0n}}\right]q^2 \tag{1}$$

for the energy of the electronic ground state (0) as a function of a distortion coordinate, q. $\mathcal{H}_q$ and $\mathcal{H}_{qq}$ are the first and second derivatives with respect to q of the electronic Hamil-

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(1) Fellow of the Alfred P. Sloan Foundation and Camille and Henry Dreyfus Teacher-Scholar.

(2) (a) Jahn, H. A.; Teller, E. *Proc. R. Soc. London, Ser. A* **1937**, *161*, 220. (b) Jahn, H. A. *Ibid.* **1938**, *164*, 117.

(3) Burdett, J. K. "Molecular Shapes"; Wiley: New York, 1980.

(4) (a) Dewar, M. J. S.; Gleicher, G. J. *J. Am. Chem. Soc.* **1965**, *87*, 3255. (b) Maier, G. *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 425.

(5) (a) Liehr, A. D. *J. Phys. Chem.* **1963**, *67*, 389, 471. (b) Pearson, R. G. *J. Phys. Chem. Soc.* **1969**, *91*, 1252, 4947. (c) Pearson, R. G. *J. Chem. Phys.* **1970**, *52*, 2167; **1970**, *53*, 2986. (d) Bartell, L. S. *J. Chem. Educ.* **1968**, *64*, 457.