Thus, for the molecules studied here, no strong preference can be expressed between a near minimal basis ab initio and a SW-Xα calculation for the interpretation of PE spectral data. However, it should be noted that we found the latter to be computationally more time consuming than the former, partly owing to difficulties encountered in converging the transition-state calculation for ionization from closely spaced ligand levels of the same symmetry.

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Theoretical Studies on the Physical Properties and Bonding of the 5d Metal Hexafluorides Using the Multiple Scattering Xα Technique

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Abstract: Nonrelativistic overlapping spheres Xα multiple scattering OSMSXα calculations have been performed on the 5d heavy metal hexafluorides MF_6, where M = W, Re, Os, Ir, Pt, and Au, and on MoF_6 and SF_6. With the aid of these calculations a consistent interpretation of the ionization potentials (IPs), electron affinities (EAs), and charge transfer (CT) electronic absorption bands for these molecules is obtained. The calculations are also shown to be successful in interpreting molecular properties related to the charge-density distributions. The method is found to be very useful in predicting trends in all the properties across the 5d series. Relativistic effects are discussed, and for the EAs it is found necessary to take into account these effects. After a semiempirical correction factor of ~1.0 eV, deduced from the molecular spin-orbit coupling constants is applied, the EAs are found to agree well with the most recent experimental estimates.

Introduction

There has been in recent years considerable interest shown in the properties of the 5d hexafluorides.[1-9] Part of this interest stems from the extraordinarily high electron affinities (EAs) (3-10 eV) of these molecules.[4] There have been a number of attempts to measure these experimentally but only upper and lower bounds have been established.[1-4] Moreover, apart from the original empirical rationalizations of Bartlett,[4] there have been no attempts to account for the relatively large EAs, in terms of their bonding features, either through actual calculation or even qualitatively. The recent success of the multiple scattering Xα technique (MSXα)[10-12] in calculating the EAs of a number of different types of atoms[13] and molecules[14-17] indicates that this method may yield results of sufficiently high quality to account for the observed EAs. Also, there have been a number of theoretical calculations on the ionization potentials[18,19] (IPs) and ultraviolet transitions[5-9,18,19] of some of these 5d metal fluorides using different methods than the MSXα technique. There has also been a previous nonoverlapping spheres MSXα calculation on WF_6[20] and one on PtF_6.[21]

Thus this series of molecules seemed to be an ideal set with which to test out our proposed overlapping spheres multiple scattering (OSMXα) method[17] both in comparison with other calculational methods and with experiment. In addition, the availability of the wave functions for this whole series of molecules has enabled us to discuss other physical properties of these molecules in a more detailed fashion than was possible previously.

Method of Calculation

The MSXα method is a nonvariational, self-consistent, one-electron technique involving the use of the Slater exchange approximation and the multiple-scattering formalism and has been described in detail elsewhere.[10-12] In addition to the experimental geometry, there are two types of theoretical pa-

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Table I. Metal Radii (bohrs) Deduced from Atomic Electron Densities and Virial Data for MF_6 Molecules

M	$R(Z-2)$[a]	$R(Z-3)$[a]	$-T/E$ ratios for models[b] I	II	III
Mo	2.338	1.992		1.0011	1.0008
W	2.678	2.172	1.0008	1.0003	
Re	2.599	2.162	1.0008	1.0003	
Os	2.554	2.153	1.0009	1.0003	
Ir	2.510	2.148	1.0008	1.0003	
Pt	2.267	2.001		1.0005	1.0009
Au	2.224	1.960		1.0005	1.0009

[a] $R(Z-n)$ is the radius inside of which there are $Z-n$ electrons as calculated using the Herman-Skillman atoms program, ref 29. [b] See discussion in text. The various models are defined as follows: model I, $R(Z-3)$ for M and $R(Z-2) = 1.310$ au for F; model II, $R(Z-3)$ for M and $R(Z-1) = 1.728$ au for F; model III, $R(Z-2)$ for M and $R(Z-2) = 1.310$ au for F; Model IV (not shown), $R(Z-2)$ for M and $R(Z-1)$ for F.

rameters which are required in order to perform MSXα calculations. These are the choice of α multiplying the Slater exchange expression and the choice of atomic sphere radii used to generate the muffin-tin potentials. The choice of α is not very crucial[22,23] for the quantities of interest. For an exact electron gas $\alpha = 2/3$, but the value of $\alpha = 0.71$, which we have used for the 5d MF_6 series, is determined by taking a weighted average of $\alpha = 0.75$ for fluorine and of $\alpha = 0.70$ for the metal atoms in the series. These two values are very nearly optimal for lighter atoms and heavier atoms, respectively.[24] The average value we have chosen to use reflects the trend toward the exact value of α with increasingly higher atomic number and may be compared to the value $\alpha = 0.72$ used by Larsson and Connolly[22] for 3d transition metal compounds.

The results obtained from MSXα calculations are very sensitive to the choice of atomic radii,[25] particularly if the muffin-tin potentials are allowed to overlap.[26,27] Unfortunately, there is as yet no universally accepted simple prescription with which to calculate the radii when overlapping spheres are used.[12,20,27] After a great deal of experimentation[28] we have adopted, as our criteria for choosing a suitable radius for a given atom, that radius within which is incorporated a certain integral value of the total electron density, as calculated using a standard Herman-Skillman atomic program.[29] For all metal atoms up to uranium it was found necessary to consider only those radii incorporating $Z-2$, $Z-3$, and $Z-4$ units of electronic charge, where Z is the atomic number. For metal atoms up to atomic number $Z = 54$, radii obtained using $Z-2$ were satisfactory, for atoms up to $Z = 86$, $Z-3$ was found to work, and for atoms with $Z > 86$, $Z-4$ was found to be superior to any other value.

Although our past experience indicated that for the 5d metals we should employ a radius corresponding to an atomic electronic charge of $Z-3$ units and a fluorine radius corresponding to either $Z-2$ units (model I) or to $Z-1$ units of electronic charge (model II), in addition we also performed calculations on WF_6 using a metal radius corresponding to $Z-2$ units of charge and the two F radii (models III and IV, respectively). These calculations, however, resulted in IP and EA values for WF_6 that were too shallow by more than 1 eV. In particular, model IV gave too much overlap and was ruled out completely on the basis of findings similar to those of Boring.[14] Calculations were not performed on the other hexafluorides using model III except for MoF_6, PtF_6, and AuF_6. For these molecules model I could not be used because the radii (Table I) would not permit the spheres to touch. Consequently a model III calculation was also performed. Again the IPs were considerably shallower than those of model II. However, this brought the IPs of MoF_6 more in line with experiment as can be seen in Table II. Since experimental IPs are not available for PtF_6 in order to make a choice between the two models, we report the IPs of PtF_6 for both models in Table III. A third possibility for PtF_6 is that, since the ground state for the Pt atom is different from the lower members of the 5d series in that it has one electron in the 6s orbital, we possibly should have used the $5d^8 6s^2$ configuration to choose the $Z-3$ radius. The difference, however, is small ($R = 2.084$ au) compared to model II and would not alter the general trends observed for the series. The radii finally used are given in Table I. Since some authors[11,12,26,27] have proposed that the virial theorem can be used to choose radii we report the viral ratios in columns 4-6 of Table I. The virial ratios for all three models are good, but the model II values are slightly closer to the ideal value of unity except for MoF_6, where model III seems to be best.

The final input parameter to be chosen is the molecular geometry. All MF_6 molecules were assumed to be octahedral with a bond distance of 1.83 Å measured by electron diffraction.[30] The same value has been used in other calculations on MF_6 molecules.[18]

The calculations were allowed to proceed until the relative difference in the potential values calculated for succeeding iterations differed by less than 1×10^{-3}. Partial wave expansions of up to $l = 4$ on the metal and the outer sphere and up to $l = 2$ on the fluorines were generally used to converge the one-electron energies to 1×10^{-5} Ry.

Ionization Potentials

A number of hexafluorides (M = S, Mo, W, and U) have been extensively studied by photoelectron spectroscopy[31] and for SF_6 there have been numerous theoretical studies culminating in the work of von Niessen et al., who employed a large Gaussian basis set in a Hartree-Fock-Roothaan type of calculation and then corrected for the effects of relaxation and electron correlation.[32] The final results of these calculations agree very well with experiment and with our overlapping spheres OSMSXα calculations in Table II. They form an excellent reference point from which to interpret the photoelectron spectra (PES) of the other hexafluorides. The PES of all the hexafluorides may be profitably discussed in terms of the atomic orbitals (AOs) of the central atom perturbing the ligand orbitals formed by the appropriate symmetry adapted linear combinations of ligand orbitals (SALCs). In SF_6 the sulfur bonding AOs are 3s and 3p and therefore interact with the SALCs of a_{1g} and t_{1u} symmetry, respectively. In the heavy-metal fluorides MoF_6 and WF_6 most of the bonding is caused by the d orbitals which interact with the t_{2g} and e_g ligand SALCs. Thus, qualitatively, one would expect that for SF_6 the ionization energies which correspond to $2a_{1g}$ and $2t_{1u}(\sigma)$ MOs would deepen and move out of the general area where we would expect the pure ligand MOs to show ionization peaks, and in the case of the Mo and W hexafluorides we would expect the ionizations due to the $1t_{2g}$ and $2e_g$ MOs to deepen. This is exactly what is found to happen in the OSMSXα transition state IP calculations which correspond very well with the experimental PES (Table II). Our interpretation is very different from the simple crystal field interpretation suggested by McDiarmid,[8] which ignores the possibility of changes in the relative order of the ligand symmetry orbitals (governed by their nodal distributions) upon molecular formation. Our assignments also differ in some respect from the assignments of Karlsson et al.,[31] which were made without benefit (or undue influence) of a theoretical model. The major difference in our interpretation compared to theirs stems from our assignments of the second band in the PES as originating from ionizations from both the $3t_{1u}$ and $1t_{2u}$ orbitals for SF_6, MoF_6, and WF_6, whereas for the latter two molecules Karlsson et al.[31] prefer to assign only the $3t_{1u}$ MO as responsible for this band even though it is very asymmetrically shaped. The assignments for

Table II. Ionization Energies (eV) of MF_6 Molecules (M = S, Mo, W)

SF_6			MoF_6				WF_6			
exptl[a]	mod I[b]	sym	exptl[a]	mod III[b]	mod II[b]	sym	exptl[a]	mod I[b]	mod II[b]	sym
15.67	15.70	$1t_{1g}$	15.07	14.97	16.37	$1t_{1g}$	15.35	15.35	15.38	$1t_{1g}$
16.93	16.95	$3t_{1u}(\pi)$	15.80	15.34	16.33	$3t_{1u}(\sigma)$	16.07	15.25	15.60	$3t_{1u}(\sigma)$
	16.95	$1t_{2u}$		15.52	16.85	$1t_{2u}$		15.90	15.93	$1t_{2u}$
			16.55	15.89	17.16	$2t_{1u}(\pi)$	16.83	16.23	16.25	$2t_{1u}(\pi)$
			17.62	16.80	17.34	$2a_{1g}$	17.22	16.35	16.71	$2a_{1g}$
18.3	18.13	$2e_g$	18.53	18.02	18.78	$1t_{2g}$	18.45 (18.8)	18.18	18.22	$1t_{2g}$
19.76	19.05	$1t_{2g}$	19.08	18.89	20.02	$2e_g$	19.36	18.84	19.52	$2e_g$
22.7	22.20	$2t_{1u}(\sigma)$								
27.0	27.15	$2a_{1g}$								

[a] Experimental values from ref 31. [b] Transition-state calculations for models as defined in Table I.

Table III. Calculated Ionization Energies of 5d Metal Hexafluorides MF_6 (eV)

	W	Re	Os	Ir	Pt		Au
sym	mod II[a]	mod II	mod II	mod II	mod II	mod III	mod II
$2t_{2g}$		11.88[b]	12.93	13.72	15.28	14.01	16.25
$1t_{1g}$	15.38	15.50	15.48	15.40	16.18	14.60	16.30
$3t_{1u}$	15.60	15.81	15.80	15.75	16.45	15.03	16.52
$1t_{2u}$	15.93	16.05	15.99	15.88	16.65	15.13	16.82
$2t_{1u}$	16.25	16.40	16.39	16.40	17.09	15.74	17.32
$2a_{1g}$	16.71	17.12	17.16	17.21	17.68	16.64	17.91
$1t_{2g}$	18.22	18.52	18.55	18.85	20.16	19.03	21.83
$2e_g$	19.52	19.96	20.17	20.40	21.53	20.29	22.85

[a] Models as defined in Table I. [b] Experimental value quoted in ref 33; IP_1 = 11.15 eV.

MoF_6 and WF_6 of the third and fourth bands were then made by them in assigning the vibrational fine structure to a_{1g} and t_{2g} vibrations. This of course is not incompatible with our assignment of the third band to ionization from a $2t_{1u}(\pi)$ orbital. Our assignment of the origin of the fourth band as from an a_{1g} orbital is also compatible with experiment. Karlsson et al.[32] assigned all the vibrations appearing in this band in WF_6 as part of an a_{1g} progression, but for MoF_6 they assigned the vibrational substructure to two vibrations. However, the experimental accuracy of the measurements is such that the substructure could also be assigned to an a_{1g} progression, thus supporting our $2a_{1g}$ assignment for the fourth band in both molecules. The broad fifth and sixth bands in the 18-19.5-eV region in both molecules are undoubtedly due to the ionization from the two bonding MOs. The extra peak in WF_6 not found in MoF_6 could be attributed to spin-orbit coupling. The relativistic DVMXα calculations of Ellis and Rosen[18] on ReF_6 show a considerable splitting of the $1t_{2g}$ MO and this, coupled with a general relativistic deepening of the $2e_g$ level, is in agreement with the observed difference between MoF_6 and WF_6 in this region of the PES.[31]

It should be mentioned at this point that, although the order of the ionization energies for WF_6 is essentially the same for both the OSMSXα and the DVMXα calculations, there is one major difference. This is that, whereas in the MSXα calculation the $2t_{1u}$ MO is almost entirely ligand 2p in character, in the DVM calculation[18] it contains considerable metal (5p for WF_6) character. This leads to a large relativistic splitting of about 0.5 eV in WF_6. Thus, one could assign the two sharp peaks (third and fourth bands) in the 16.7-17.5-eV region as due to a split of the $2t_{1u}$ nonrelativistic orbital into 6^- and 8^- relativistic orbitals. The ionization of the $2a_{1g}$ orbital in WF_6 would then be regarded as the 18.4-eV peak and the $1t_{2g}$ ionization as the new structure at about 18.8 eV (not found in MoF_6). The shift from 17.62 eV in MoF_6 of the $2a_{1g}$ ionization to 18.4 eV in WF_6 would then be assigned to a relativistic deepening of the $2a_{1g}$ level in WF_6. Unfortunately, Ellis and Rosen[18] used a different (larger) basis set for their relativistic calculations so it is not possible to extract from their work the effect of relativity on the levels which do not split. However, their calculations[18,19] clearly demonstrate that relativistic effects cannot be ignored in the interpretation of the spectroscopic properties of heavy-metal complexes.

Table IV. Electron Affinities of MF_6 Molecules (eV)

M	mod I[a]	mod II[a]	cor EAs[d]	exptl[e]
S	0.53		(0.53)	0.5 ± 0.2
Mo	(4.50)[b]	(5.87)[c]	(4.79)	5.36
W	4.35	3.90	5.07	5.1 − 0.5 or +0.2
Re	5.27	4.98	6.27	(6.14)
Os	6.17	5.97	7.32	(7.19)
Ir	6.96	6.86	8.31	(8.24)
Pt	(7.59)[b]	8.55	9.06	9.3
Au	(8.34)[b]	9.54	10.05	(>10.0)

[a] The two major models as described in the text and in Table I. [b] Values in parentheses are calculated using model III as discussed in text. [c] See text and Tables I and II. The model II value for MoF_6 was tentatively ruled out on the basis of the virial ratio and depth of the theoretical IPs. [d] Corrected for relativistic effects as discussed in text. Tabulated values correspond to model II except for S (model I) and Mo (model III). [e] Best available experimental values as quoted in ref 1 and described in text. Values in parentheses are not known experimentally but see text for discussion. The value tabulated here for SF_6 reflects the range of experimental values quoted in ref 14.

OSMSXα calculations on the IPs of the rest of the 5d hexafluorides are given in Table III. The only other experimetal result is an unpublished value for the first IP of ReF_6 measured by Brundle and quoted by McDiarmid.[33] Our calculated value is 0.73 eV deeper than this value without relativistic correction. The first IP increases with atomic number, but the increment as we ascend the series is not constant, as was found for the EAs (Table IV). As expected, the IPs of the ligand orbitals do not change much across the first four members of the series. Model II, however, predicts a sharp drop of 0.6-0.9 eV on passing from Ir to Pt. It can be seen by comparing the results of cal-

Table V. Percent Metal Character in the $2t_{2g}$ Orbital of MF_6's as Estimated from Relativistic Splittings (All Energies in eV)

	Mo	W	Re	Os	Ir	Pt	Au
atomic d[a] relativistic splittings	0.2532	0.9358	1.0321	1.2756	1.4182	1.5809	
% metal d estimated[b] in $2t_{2g}$		69.5	63.0	51.0	45.8	41.6	
theoretical[c] $X\alpha$ % d character in $2t_{2g}$	72.0	71.5	67.0	60.6	57.5	42.9	23.1

[a] Values taken from ref 29, p II-13. The values for Re and Ir had to be interpolated as only values for even Z were quoted. [b] Deduced from taking a constant relativistic molecular splitting value of 0.65 eV for entire 5d series as suggested in ref 5 and then calculated using eq 1 as suggested in text. [c] Taken from a population analysis which uses the same renormalization procedure discussed in ref 17b.

culations using model II with those of model III (Table III) that the IPs of PtF_6 are very sensitive to changes in the muffin-tin radii. The MS$X\alpha$ model II prediction that the IPs of PtF_6 are deeper than those of the lower members of the series is also contrary to the predictions of the DVM$X\alpha$ calculations, which predict that the first three ligand IPs are considerably lower for PtF_6 than for IrF_6[18] in agreement with our model III.

Electron Affinities

The results of our transition-state calculations on the EAs of the 5d metal hexafluorides are given in columns 2 and 3 of Table IV. Before comparing our nonrelativistic calculations with experiment we have attempted to make very crude relativistic corrections. The corrected values for model II are reported in column 4 of Table IV. The corrections were made by taking differences between the nonrelativistic and the relativistic energies of the 5d orbitals from atomic calculations for each metal atom[29] and multiplying these by the $X\alpha$ fraction of the metal character (given in Table V) in the molecular $2t_{2g}$ orbital. The net effect of this correction is to increase the magnitude of the EA by approximately 1 eV.[47]

As a demonstration that the fraction of metal character given by the OSMS$X\alpha$ method is reasonable, we have used eq 1 to obtain the percentage metal character.

$$\%\ \text{metal character} = \frac{\text{experimental molecular spin orbit splitting}}{\text{theoretical atomic spin orbit splitting}} \qquad (1)$$

For the observed spin-orbit splitting constant we have used only one value of $\sim 5.2 \times 10^3$ cm^{-1} (0.65 eV) for all the 5d hexafluorides as suggested by Moffitt et al.[5] and the theoretical atomic d splitting values from ref 29. The results are given in row 2 of Table V. The agreement with the corresponding quality calculated using the OSMS$X\alpha$ molecular wave function directly is quite remarkable. These calculations clearly show that the nearly constant spin-orbit splitting deduced from the electronic spectra of the 5d metal hexafluorides[5] is due to a decrease in the amount of metal character in the $2t_{2g}$ orbital with increase in atomic number which counterbalances almost exactly the corresponding increase in the metal spin-orbit splitting as estimated from the relativistic atomic calculations.[29]

There have been numerous attempts to establish experimentally precise values of the EAs of the 5d hexafluorides. Although there is general agreement that the EAs of these hexafluorides are very large (3.5-9.5 eV), there is considerable disagreement among different workers[1-3] on the actual magnitudes of the individual EAs. Compton et al.[1] reviewed critically in 1978 previous measurements on the EAs and reported new measurements using a crossed beam collisional ionization method with alkali metal atom beams. Mathur et al.[34] have also carried out similar crossed beam collisional ionization experiments and obtained virtually identical results. Consequently the experimental data which we have chosen (Table IV) to compare with our theoretical calculations for MoF_6, WF_6, and PtF_6 are taken from Compton's tabulation (Table 4 of ref 1). There are no direct determinations for the hexafluorides Re, Os, and Ir, and the values given in Table IV were obtained by assuming a constant increment per unit increase of atomic number as suggested by Bartlett.[4] The value of 1.05 eV per unit Z increase is larger than that originally suggested by Bartlett[4] since it was obtained using his revised value for the EA of PtF_6.[35]

The excellent quantitative agreement with the experimental estimates of the EAs of ref 1 and 35 for the 5d hexafluorides is probably fortuitous to some extent, but it favors the higher values in the literature rather than the lower limits favored by some experimentalists.[3] Most of the experimental work favors a higher EA for MoF_6 than for WF_6,[1,2,8] whereas after making relativistic corrections the calculations predict the MoF_6 EA to be 0.3 eV lower than for WF_6. Since we have made no attempt on these molecules to optimize 4d metals with respect to the 5d (down a group instead of across a series), this result is not unreasonable. Boring[14] encountered similar problems in comparing SeF_6 to TeF_6.

In all the 5d metal hexafluorides the captured electron goes into the $2t_{2g}$ antibonding level which is relativistically split into $2t_{2g}(3/2)$ and $2t_{2g}(1/2)$. The lower $2t_{2g}(3/2)$ level becomes filled in IrF_6^-, and in PtF_6 the electron attaches into the upper $2t_{2g}(1/2)$ level. This population effect tends to offset the disparate gap between the EA of IrF_6 and PtF_6 ($\sim$1.7 eV) found in our nonrelativistic model II calculations (column 3 of Table IV). In turn the decreasing amount of metal character in the $2t_{2g}$ level (Table V) across the series appears to offset an increasing relativistic effect noted for the atoms[29] (Table V) in ascending the series so that, in the molecules, the splitting of the $2t_{2g}$ level remains fairly constant.

Charge-Transfer Spectra

There have been a number of successful MS$X\alpha$ calculations on the transition energies of ligand to metal charge transfer bands of metal complexes.[11,12,36-39] However, a previous MS$X\alpha$ calculation on WF_6 using nonoverlapping spheres[20] gave allowed transitions almost 1.7 eV too low compared to experiment. This result was attributed to "an inherent error in the $X\alpha$ method" and was linked to errors in the calculated differences between the 5d(W) and 2p(F) atomic energy levels. Our OSMS$X\alpha$ calculations gave similar low values for the transition energies, but in view of the success of our calculations in the IPs and EAs it seems unlikely that the discrepancy can be attributed to errors in the one-electron energies. Rather the error seems to be related to the small relaxation energies ($\sim$0.5 eV) associated with transition-state calculations on electronic transitions compared to the much larger values (±3.6 eV) found in our transition-state calculations on the IPs and EAs.

It is often proposed that the energy (ΔE_{CT}) of a charge-transfer band can be related to the IPs and EAs by an equation of the form[2,8]

$$\Delta E_{\mathrm{CT}} = I - \mathrm{EA} - Q \qquad (2)$$

where Q is a correction factor incorporating the attraction of the Coulomb hole as well as relaxation factors. It is possible that for all the CT transitions of one molecule and also for all the CT transitions in a related series of molecules Q could be

Table VI. Assignments of Charge-Transfer Bands for MoF_6 and WF_6 (Energies in eV)

MoF_6				WF_6		
exptl ν^a	ϵ^a	calcd^b	$X\alpha$ assn	exptl $\nu^{a,c}$	calcd^b	$X\alpha$ assn
5.90	500	5.87	$1t_{1g} \rightarrow 2t_{2g}$	7.23	7.20	$1t_{1g} \rightarrow 2t_{2g}$
6.54	2200	6.60	$3t_{1u} \rightarrow 2t_{2g}$	8.05	7.92	$3t_{1u} \rightarrow 2t_{2g}$
			$1t_{2u}$			$1t_{2u}$
7.12	5000	7.32	$2t_{1u} \rightarrow 2t_{2g}$	8.60	8.68	$2t_{1u} \rightarrow 2t_{2g}$
8.62	50	8.42	$2a_{1g} \rightarrow 2t_{2g}$	8.94 (w)	9.07	$2a_{1g} \rightarrow 2t_{2g}$
9.22	<20	9.33	$1t_{2g} \rightarrow 2t_{2g}$	10.03 (w)	10.28	$1t_{2g} \rightarrow 2t_{2g}$
10.04	600	9.88	$2e_g \rightarrow 2t_{2g}$	11.05	11.21	$2e_g \rightarrow 2t_{2g}$
>10.86	≥3000			11.75^c		R
		11.01^d	$1t_{1g} \rightarrow 3e_g$	12.60^c	12.60^d	$1t_{1g} \rightarrow 3e_g$
		11.74^d	$3t_{1u} \rightarrow 3e_g$	13.50^c	13.32^d	$3t_{1u} \rightarrow 3e_g$

[a] Experimental values from McDiarmid, ref 8. [b] Calculations using eq 2 and experimental IPs from ref 31. $Q = 4.40$ eV for MoF_6 and 3.05 eV for WF_6. [c] Experimental results from ref 40. [d] The EA of the $3e_g$ level was calculated using the same relaxation energy as was found for the $2t_{2g}$ level.

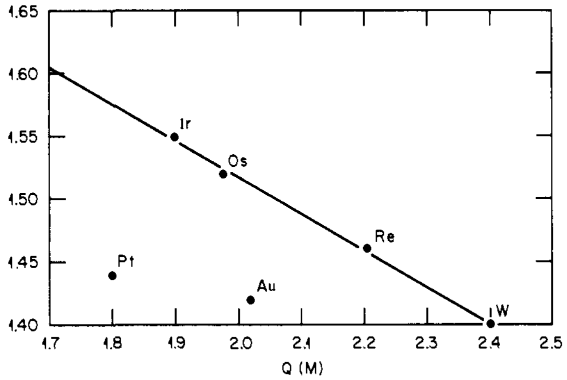

Figure 1. Allred-Rochow electronegativities (EN) plotted vs. the calculated effective metal charges Q(M) for the MF_6 series.

Table VII. Calculated MF_6 UV Transition Energies (eV)

	Re	Os	Ir	Pt	
transition^a	mod II	mod II	mod II	mod II	mod III
$(2t_{2g} \rightarrow 3e_g)^b$	5.75	5.60	5.37	4.97	
$(1t_{1g} \rightarrow 2t_{2g})$	6.18	5.11	4.04	4.07	2.49
$(3t_{1u} \rightarrow 2t_{2g})$	6.49	5.43	4.39	4.34	2.92
$(1t_{2u})$	6.73	5.62	4.52	4.54	3.02
$(2t_{1u} \rightarrow 2t_{2g})$	7.08	6.03	5.04	4.98	3.63

[a] Top four (allowed) CT transitions were calculated using the theoretical IPs (Table III), theoretical EAs (Table IV), and $Q = 3.05$ eV in eq 2. [b] Theoretical estimates of the energy regions in which the $(2t_{2g} \rightarrow 3e_g)$ d-d transitions are predicted to lie. The estimates were made from the calculated $X\alpha$ ΔE $(2t_{2g}, 3e_g)$ one-electron energy differences with an added relaxation factor of ~0.5 eV. Note also that the MS$X\alpha$ method gives only a weighted average of the multiplet splittings.

a constant. Very good experimental data has recently become available for the CT transitions of WF_6,[8,40] and they provide an excellent opportunity to test this equation. The results are given in Table VI. For WF_6 the experimental IPs are used along with the theoretical corrected EA. A fit of theory to experimental transition energy ΔE_{CT} for the first CT band then gave a Q of 3.05 eV. This value was then used to obtain very good agreement between theory and experiment for seven out of the next eight transitions experimentally observed. The transition observed at 11.75 eV could not be fitted by eq 2 and is therefore assigned as a Rydberg transition in agreement with the assignment given in ref 40. However, our other assignments differ considerably from those qualitatively suggested in ref 40, in which a one-to-one correspondence between the spectra of WF_6 and UF_6 was assumed. Our $X\alpha$ calculations of UF_6[28] and WF_6 do not show such a one-to-one correspondence in the order of either the one-electron energies or the calculated IPs. Our assignment of the fouth IP as originating from a $t_{1u}(\pi)$-type ligand orbital is in agreement with our assignment of the strong CT band at 8.60 eV in WF_6 as an allowed $2t_{1u} \rightarrow 2t_{2g}$ transition. Also our MS$X\alpha$ calculated energy gap between the unoccupied $3e_g$ and $2t_{2g}$ levels of 5.49 eV for WF_6 fits quantitatively the assignment of the last two transitions as excitations from the first two occupied energy levels ($1t_{1g}$ and $3t_{1u}$) to the second unoccupied energy level ($3e_g$). High-quality data on MoF_6 is also available,[8] but only up to 10.5 eV. It was hoped, but for no fundamental reason, that the same Q value used for the 5d hexafluorides could be used for this 4d hexafluoride also, but this hypothesis was found to be untenable, and a Q value of 4.40 eV (from fitting the first transition) had to be used. The agreement with McDiarmid's experimental work[8] is then also very good. Again, our assignment of the IP at 16.5 eV as originating from a $2t_{1u}(\pi)$ ligand orbital is corroborated by our assignment of the very strong UV band at 7.12 eV to an allowed $2t_{1u} \rightarrow 2t_{2g}$ transition and the next transition (8.29 eV), which is very weak (Table VI), as originating from a $2a_{1g}$ orbital.

We have used the Q value obtained for WF_6 to calculate the charge-transfer transitions of the other 5d hexafluorides (Table VII). The predicted trend of a movement to lower transition energies with increase in atomic number of the central atom is in agreement with the experimental work on these hexafluorides.[5] The detailed assignments, which differ somewhat from previous assignments,[6,7,9] are reported elsewhere.[28]

Charge Densities and Physical Properties

It is interesting to compare the electronegativities (EN) of the 5d metal atoms with the calculated net positive charges Q(M) on the metals in the 5d hexafluorides. Here $Q(M) \equiv Z(M) - \rho(M)$ where Z(M) is the atomic number and ρ(M) is the $X\alpha$ calculated total charge density of the metal M. For the first four members of the series there is (Figure 1) a linear relationship between Q(M) and the Allred-Rochow electronegativities.[41] However, for Pt and Au the relationship breaks down. A plot of Q(M) against the calculated model II uncorrected EAs also shows (Figure 2) a smooth curve relationship up to Pt, but for Au Q(M) is much larger than the value obtained by extrapolating the smooth curve.

These deviations raise the question of whether the calculated Q(M) values are reliable. Unfortunately, the only measured physical properties of the 5d hexafluorides which might be related to the charge-density distributions are the vibrational frequencies[42,43] and the molar volumes.[4]

The totally symmetric stretching frequencies (ν_1) both for the MF_6 and MF_6^- series fall off considerably with increase in metal atomic number.[42,43] Intuitively one is tempted to relate this drop to a decrease in the bond orders across the series for the $\pi(2t_{2g})$ antibonding orbital. Since the bond order is a

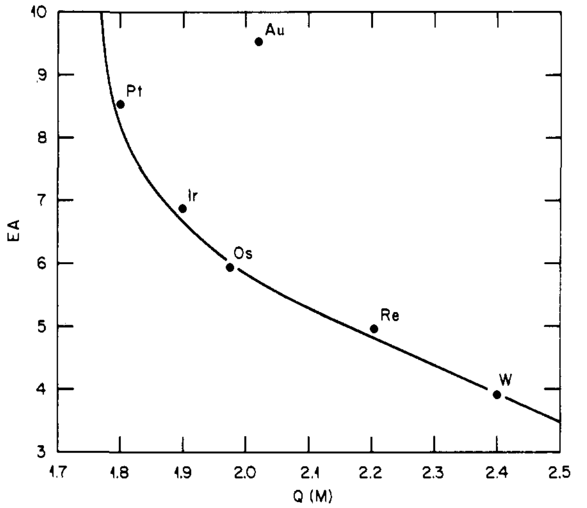

Figure 2. (●) Calculated model II uncorrected EAs plotted vs. the calculated effective metal charges $Q(\mathrm{M})$. (—) Smooth curve connecting the calculated points (W through Pt).

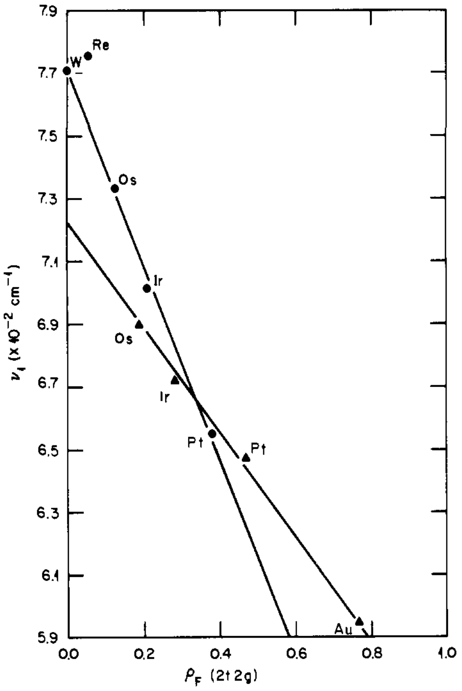

Figure 3. Plot of the observed ν_1 frequencies vs. $\rho_F(2t_{2g})$, the calculated ligand population densities in the antibonding $\pi(2t_{2g})$ orbital: (●) MF_6; (▲) MF_6^-.

quantity unavailable from our $X\alpha$ calculations we show (in Figure 3) the ligand electron densities in the antibonding $\pi(2t_{2g})$ orbital, $\rho_F(2t_{2g})$, plotted against the observed ν_1 frequencies. The relationship is indeed linear for both the MF_6 and MF_6^- series. Kim et al.[43] have carried out force-field calculations on a number of MF_6 molecules. They find that the force constant K for the M-F bond changes very little across the 5d hexafluoride series and that the drop in the observed frequency is due almost entirely to a drop in the nonbonding repulsion force constant F which should be related to a decrease in total charge density on the fluorine atoms across the series. Figure 4 shows that there is a very good linear relationship between their F values and the OSMSXα calculated $Q(\mathrm{F})$ values, where $Q(\mathrm{F})$ is the net excess electron density on fluorine, i.e., $Q(\mathrm{F}) = -Q(\mathrm{M})/6$. This we feel demonstrates that our calculations are at least producing the right trend across the series up to Pt.

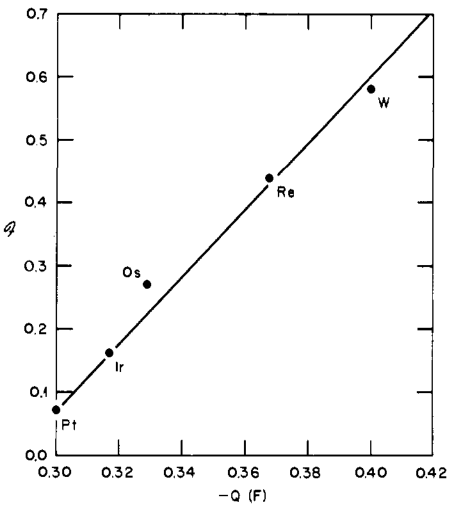

Figure 4. Nonbonding repulsion force constants F plotted vs. the net excess electron densities $Q(\mathrm{F})$ on fluorine for the MF_6 series.

Bartlett[4] commented that the slight decrease in the van der Waals radius of the ligands with increasing atomic number of the central atom up to Pt, as measured by the molar volume, is evidence that the fluorine electron density decreases across the series as predicted by the calculations ($\rho(\mathrm{F})$ in Table VIII). Similarly the smaller molar volume of MoF_6 compared to WF_6[4] is evidence that the fluorine electron density is greater in the latter molecule than in the former, again in agreement with the calculations.

Bartlett[4] attempted to rationalize the increase in EA with atomic number of the 5d hexafluorides in terms of an increase in the polarity of the $\sigma(2e_g)$ M-F bond causing an electron deficiency on the ligands which is responsible for deepening the energy of the partially filled ligand $\pi(2t_{2g})$ orbitals into which it was assumed the added electron went. Because of the extensive mixing of the metal and ligand orbitals, the bonding picture obtained from the OSMSXα calculations is more complicated than this simple model. Thus, whereas the calculations support the original idea that the $\sigma(2e_g)$ bond is increasingly polarized toward the metal with increasing atomic number (see row 2 of Table IX), the electron density in the π bonding orbital ($1t_{2g}$) is even more polarized as the atomic number increases (row 3 of Table IX). It is surprising that, in spite of this considerable increase in electron transfer to the metal from the fluorine, the IPs of both the two bonding orbitals ($1t_{2g}$ and $2e_g$) increase by less than 2 eV across the series (Table III). On the other hand, the IP and EA of the antibonding $\pi(2t_{2g})$ orbital (Tables III and IV) increase considerably across the series. In fact, there is, as previously noted, a smooth curve relationship between the net electron density on the fluorines $Q(\mathrm{F}) = -Q(\mathrm{M})/6$ and the EAs (Figure 2) for W up to Pt. This smooth curve relationship tends to support the idea of Bartlett[4] that the increase in EA is due to an electron deficiency on the ligands. However, an alternative explanation which we prefer is to relate the increase in EA to the change in electron density on the metal atom. As the electron density of the fluorine decreases, there is of course a concomitant increase in the density on the metal. This increase takes place mostly in the 5d orbitals (Table VIII). One can then argue that a major factor in the increase of the EA is the deepening of the atomic 5d energy levels[29] with increase in atomic number caused by imperfect shielding of the atomic d orbitals as they are filled.

For a pure d shell the atomic calculations show for the $5d^{n-1}6s^2$ configuration a drop of 1.30 eV per unit increase in atomic number up to Hg.[28,29] The molecular OSMSXα calculations indicate that, because the increasing polarity of the M-F bond

Table VIII. Total Valence Electron Density Analysis for MF_6 Molecules

atomic orbital	W	Re	Os	Ir	Pt	Au
6s	0.168	0.181	0.193	0.207	0.143	0.140
6p	0.193	0.211	0.233	0.257	0.163	0.157
M 5d	2.942	4.141	5.349	6.394	7.760	8.566
5f	0.213	0.210	0.203	0.197	0.114	0.099
4g	0.056	0.051	0.048	0.045	0.021	0.017
2s	1.960	1.962	1.963	1.964	1.982	1.986
F 2p	5.421	5.380	5.340	5.326	5.294	5.328
3d	0.023	0.025	0.027	0.027	0.024	0.023
$\rho_\nu(M)$[a]	3.572	4.794	6.025	7.100	8.200	8.980
$\rho_\nu(F)$[a]	7.404	7.367	7.330	7.317	7.300	7.337

[a] $\rho_\nu(M)$ and $\rho_\nu(F)$ are the sums of the individual valence orbital electron densities. $Q(M) \equiv Z_\nu(M) - \rho_\nu(M)$ where $Z_\nu(M)$ is the metal atomic number minus the number of core electrons. $Q(F) \equiv 7 - \rho_\nu(F)$ or $Q(F) = -Q(M)/6$. The Q values used in the figures are calculated using $Q(M) \equiv Z(M) - \rho(M)$, which is equivalent to the $Q(M)$ defined here.

Table IX. Metal 5d Orbital Density Analysis in MF_6 Molecules

orbital	W	Re	Os	Ir	Pt	Au
$2t_{2g}(\pi)$	0.000	0.670	1.212	1.725	1.716	1.155
$2e_g(\sigma)$	1.260	1.400	1.560	1.688	2.024	2.384
$1t_{2g}(\pi)$	1.482	1.872	2.370	2.772	3.846	4.842
total	2.742	3.942	5.142	6.185	7.586	8.381

in the two bonding MOs (Table IX) is not completely offset by the polarization toward the ligands in the partially filled antibonding ($2t_{2g}$) orbital, there is a net increase in electron density on the metal of slightly greater than one d electron per unit increase in Z number (Tables VIII and IX). This increase corresponds very well to the increase in EA of about 1.1 eV as we go across the 5d hexafluoride series. Also this alternate explanation accounts for the increase in the EA of AuF_6, an effect which cannot be readily explained by relating the EA to the fluorine density.

In AuF_6 the calculated fluorine electron density is much higher than the smooth curve relationship in Figure 2 would indicate. In fact the fluorine electron densities for both PtF_6 and AuF_6 are considerably higher than would be expected by a linear extrapolation of the fluorine densities for the lower members of the series (Figure 2), apparently because for the lower members the fluorine electron densities are partially transferred to the metal 6s and 6p orbitals, which become increasingly populated up to Ir. Then there is a sharp drop in the populations (see rows 1 and 2, Table VIII). This occurs presumably because of the same electron-pairing energy terms responsible for making the ground-state atomic configurations of Pt and Au $5d^n6s$ rather than the $5d^{n-1}6s^2$ configuration found for the lower members. The resultant increase in the fluorine densities for PtF_6 and AuF_6 is not, however, manifested in either a lower EA or IP. Thus, although the EAs of the first four members of the series are apparently directly related to the electron densities on the ligands (Figure 2), in accordance with Bartlett's rationalization,[4] the EAs of the last two members are not. The anomalous behavior of PtF_6 and AuF_6 is also demonstrated by the plots shown in Figures 1 and 3. The calculations nonetheless predict a very high EA for AuF_6 in agreement with Bartlett's[4] suggestion that AuF_6, were it to be made, would probably be capable of oxidizing krypton.

Discussion

The calculations presented here provide considerable insight into the reasons why the 5d hexafluorides have very high EAs and how the orbital accepting the electron in these molecules is different from the electron-accepting orbital in other hexafluorides such as SF_6 and UF_6. In the group 6 hexafluorides the electron-accepting orbital is totally symmetric and quite delocalized. It is formed by an interaction between the ns orbital of the central atom ($n = 3$ for sulfur) and the 2s and 2p fluorine ligand orbitals. For sulfur this interaction is very strong as is shown by the magnitude of the lowering of the $2a_{1g}(\sigma)$ bonding orbital, which has an ionization energy of 27.0 eV (Table II). This interaction results in a correspondingly large destabilizing of the $3a_{1g}$ antibonding orbital, into which the attaching electron goes. Although the destabilization is not enough to make the orbital unbound, it is responsible for the relatively low EA of SF_6. The interaction is less for the higher members of the group and leads to EAs of ~3.0 eV for SeF_6 and TeF_6.[14]

In the 5d hexafluorides the main bonding interactions are between the incomplete 5d shell and the fluorine 2p SALCs of e_g and t_{2g} symmetry. Since the overlap between the 5d orbitals and the ligand SALCs is not nearly as great as the interaction in SF_6 the stabilization of the bonding $2e_g$ and $1t_{2g}$ orbitals is much less, as is indicated by the IPs of the orbitals in WF_6 (Table II). The destabilizing effect on the antibonding orbital is also small so that the EA of the $2t_{2g}$ orbital, into which the electron goes, is much higher in the 5d hexafluorides than in SF_6.

There is in addition an overall increase in the EA of these molecules due to relativistic effects. We have made a rough estimate that the relativistic effect is 1.0 eV for all the 5d hexafluorides. As discussed above this is in agreement with Moffitt's finding[5] of a constant amount of spin-orbit coupling across the series and, according to our calculations, is due to a decrease in the percentage metal character in the $2t_{2g}$ orbital across the series.

In the case of uranium hexafluoride the main bonding is between the metal 5f orbitals and ligand SALCs of a_{2u}, t_{2u}, and t_{1u} symmetry. The interaction between these SALCs and the 5f orbitals stabilizes orbitals of this symmetry which results in a different order in the energy levels of UF_6 than in WF_6 so that there is not a one-to-one correspondance between the IPs of the two molecules as assumed by Rianda et al.[40] Nonrelativistic MSXα[14,28] calculations predict that electron attachment to UF_6 takes place into an a_{2u} orbital which is almost entirely f electron in character. Very recent OSMSXα calculations by Boring and Wood,[44] who included relativistic corrections within the multiple scattering formalism, predict that the EA of UF_6 is decreased by about 1 eV compared to the nonrelativistic result.[14]

Conclusions

The OSMSXα calculations on the IPs and EAs of the 5d hexafluorides are in remarkably good agreement with experiment and reinforce previous findings that this method can provide very useful information concerning EAs which are very difficult to measure accurately. In addition to the values of the EAs, the calculations provide a great deal of information concerning the nature of the bonding in these molecules and provide an explanation, in terms of the interaction between the central atom orbitals and the SALCs of the ligand orbitals, for the wide range of EA values found for different hexafluoride molecules.

The size of the relativistic corrections which had to be made to the nonrelativistic calculations presented here points to the desirability of performing proper Dirac-Slater relativistic calculations within the MSXα formalism, similar to that proposed by Boring and Wood,[44,45] for molecules containing atoms of the fifth and higher rows of the periodic table.

In contrast to the success of the MSXα method in calculating the IPs and EAs, the method failed in the calculation of the transition energies of the charge-transfer bands of the 5d metal hexafluorides. This failure may be associated with the use of the half-occupation transition state method rather than an inherent error in the MSXα method as previously claimed.[20] The availability of high-resolution electronic spectra and electron-impact studies such as those recently reported for WF_6[40] on other hexahalide systems would be of great help in further theoretical investigations of this problem. Very recent MSXα calculations on the CT transitions of UF_6[44] and on UCl_6[46] give transition energies which are also too low.

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