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THE ELECTRONIC SPECTRA OF THE HEXAFLUORO COMPLEXES OF THE TRANSITION METALS

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A. INTRODUCTION

Within the last fifteen years great progress has been made in the study of the electronic spectra of the hexafluoro complexes of the transition metals. A number of interesting systems remain to be investigated, notably the remarkable CuF_6^{2-} anion of the 3*d* series [1], the MF_6 compounds of the 4*d* series and the ReF_6^- and AuF_6^- species [2,3] of the 5*d* block, but by and large the spectroscopic behaviour of MF_6 systems of the three *d*-electron transition series is now quite comprehensively covered. A short time ago we reviewed the situation as regards the first transition series [4], and more recently have surveyed the position for the second and third series [5]. In these reviews we confined our attention to systems containing discrete MF_6 entities, rather than those merely approximating to octahedral coordination, and we here follow a similar limitation. In our earlier coverage we described in some detail the spectroscopic features of numerous individual complexes, as well as presenting a more general picture of the behaviour of the respective transition series. However, in order to prevent unnecessary recapitulation of previous material we propose to concentrate attention here on the interpretation of the values of the ligand field parameters which may be obtained from the electronic spectra of hexafluoro species in general, and especially to consider what information may be derived from the nephelauxetic and relativistic ratios, and from the positions of ligand—metal charge-transfer bands.

In this consideration we shall follow as before an essentially phenomenological approach. This is not because we believe the molecular orbital description of such species to be inapplicable, but because, as we have previously indicated, we feel that MO theory, even in its more sophisticated versions, has as yet little predictive value in regard to electronic spectral excitation energies. Consequently we shall utilise the interpretation of *d—d* spectra in terms of the familiar strong ligand field scheme, with the inclusion of spin-orbit coupling where appropriate, whilst for the charge-transfer transitions we shall make use of the usual qualitative MO scheme for octahedral complexes, in conjunction with the concept of optical electronegativity. We have already described in some detail the basic theory employed [4—6] and this will not therefore be rehearsed again.

It is nevertheless appropriate to consider at this point a number of features which make a study of the electronic spectra of transition metal hexafluorides particularly rewarding, or potentially so. To begin with many high, and often almost inaccessible, oxidation states of the transition metals are stabilised, almost uniquely, by the fluoride ligand, and it is thus frequently possible to obtain data for d^n configurations representing otherwise inaccessible valencies. Moreover, the fluoride ligand occupies a very low position in the spectrochemical series, thus leading to smaller values of Dq than for other ligands, and the majority of the *d—d* bands which occur for a given system, therefore, usually lie within an accessible region of the spectrum. Fortunately, this effect is accompanied by a very high optical electronegativity for F^-, so that the ligand—metal charge-transfer transitions tend to occur at relatively high energies, thus again facilitating the observation of the *d—d* bands.

On the debit side though many fluoride complexes, especially those of the higher oxidation states, are of limited stability in air or in the presence of moisture, and are either insoluble in, or decomposed by, the usual solvents. Nevertheless, these materials can be effectively studied by means of diffuse reflectance spectroscopy, and although accurate quantitative information regarding intensities cannot be obtained, it is normally possible to assign most of the observed bands and to derive the ligand field fitting parameters, Dq and B.

In this present review we consider first of all the interpretation of the derived values of these parameters for the hexafluorides of the three transition series. In this we focus attention chiefly on the values of the Racah parameters, B, obtained for the various systems, and on the values of the nephelauxetic ratio, β ($= B_{\text{complex}}/B_{\text{free ion}}$), thence deduced. More particularly we endeavour to indicate the extent to which these β values can be used to assess the extent of covalency — or metal—ligand mixing — in the various species, and we also investigate whether any useful information can be derived concerning the effective positive charge on the metal. As regards the splitting parameter,

Dq, there is much less information to be gleaned. Dq is effectively a measure of the difference in metal—ligand mixing between the σ-bonding e_g level and the π-bonding t_{2g} level, and is therefore not a primary measure of the extent of covalency. We therefore restrict ourselves to indicating that for hexafluorides this parameter follows the usual trend $Dq(3d) < Dq(4d) < Dq(5d)$, and for a given metal $Dq(\text{M}^{n+}) < Dq(\text{M}^{n+1+}) < Dq(\text{M}^{n+2+})$ etc.

In the 5d series it is often possible to obtain reasonable estimates for the value of the effective spin-orbit coupling constant from the optical spectra. Indeed in some $5d^4$ and $5d^5$ systems the spin-orbit splitting of the ground state manifold may be observed directly [7, 8]. In principle therefore one may obtain values for the relativistic ratio β^*, $(= \zeta_{\text{complex}}/\zeta_{\text{free ion}})$, but in practice the information derived is of only semi-quantitative value since the free ion ζ values are not known experimentally and have to be deduced by extrapolation.

Finally we examine the information obtainable from the charge-transfer spectra. In most cases it is possible to ascertain with certainty the position of the onset of these transitions, even from diffuse reflectance data, and thus to derive values for Jørgensen's [9] optical electronegativity parameter, χ_{opt}. Attention is therefore concentrated on the variation of this parameter within a given transition series, and on its dependence on the oxidation state of the metal. More specifically the relationship subsisting between the nephelauxetic ratio and optical electronegativity is further examined. In the 5d, and to a lesser extent 4d, series, the value of the spin-orbit coupling constant becomes comparable with Dq; consequently it is necessary to include spin-orbit as well as spin-pairing corrections in deriving the value of χ_{opt} from the energies of the lowest charge-transfer bands, and we have therefore described the important changes in the values of the optical electronegativities which result for some 5d element oxidation states.

B. INTERPRETATION OF LIGAND FIELD PARAMETERS

(i) The nephelauxetic ratio, β

The ligand field analysis of the d—d spectra of transition metal hexafluoro complexes is most readily accomplished by the use of the strong field O_h repulsion matrices given by Tanabe and Sugano [10,11]. Three parameters are in fact involved, namely, Dq, which measures the difference in the one electron core energies between the e_g and t_{2g} metal orbitals, and the Racah electrostatic repulsion terms, B and C. Whilst it is possible in principle to allow B and C to vary independently, in practice this tends to lead to widely varying values of these parameters for a series of chemically similar species, and we have therefore normally assumed fixed values for the ratio C/B, corresponding to the free ion situation. The available independent quantities are therefore Dq and B, but for the latter it is usually not possible to distinguish between e_g and t_{2g} electron contributions to the repulsion terms. In a few cases, d^3 and d^8 configurations, it is feasible to make this distinction and $B_{55}(t_{2g} - t_{2g})$ and $B_{33}(e_g - e_g)$ values respectively can be estimated, as well as the usual $B_{35}(e_g - t_{2g})$ parameter. However, unless the B_{35} and B_{55} or B_{33} values are markedly different no great reliance may be placed upon them because of the often appreciable off-diagonal repulsion matrix elements connecting the $t_{2g}^p e_g^q$ configurations differing in orbital occupation numbers. In general therefore in the Tables which follow the B values are B_{35} quantities except where otherwise indicated, the only major exception being those species of the 5d series possessing well defined t_{2g}^n ground states for which the B parameter is clearly essentially a B_{55} quantity.

From the derived B values the nephelauxetic ratios can be found as long as the free ion B parameters are known. Theoretical calculation of the latter is inadequate since the failure to allow for correlation effects leads to values some 30% too large, but B can be obtained empirically from the Slater—Condon F_k parameters deduced from the atomic spectra of the appropriate metal in the required oxidation state. A number of compilations of F_k or B values are now available including those listed by Tanabe and Sugano [11], and those given by Oleari and co-workers [12,13], but a semi-empirical relationship based on work by Racah [14] and developed by Jørgensen [15] has been widely used for the calculation of free ion B values. For the higher oxidation states these various quantities are in tolerably good agreement, but for the neutral atoms the Jørgensen—Racah relationship leads to markedly smaller free atom B values than the experimental values. As will be evident later this is of some consequence when attempting to use experimental B_{complex} values to estimate effective positive charge on the metal.

Basically the nephelauxetic effect may be considered to reflect two covalent contributions [16]. On the one hand there is central field covalency, due to the reduction of the effective positive charge on the cation by the screening of the d^n configuration, and on the other symmetry restricted covalency arising from the participation of the metal e_g and t_{2g} orbitals in molecular orbital formation with the appropriate symmetry adapted ligand combinations. It is not easy though to separate these contributions merely from a knowledge of β alone. Thus Jørgensen has demonstrated an approximate proportionality between $B_{\text{free ion}}$ and $(z + Z)$ where z is the ionic charge and Z a small constant, whereas in a complex the corresponding proportionality is to $a^4(z_{\text{eff}} + Z)$, where z_{eff} is the effective cationic charge and a the Stevens' [17] delocalisation coefficient. Thus the central field effect operates by reducing z to z_{eff} and the symmetry restricted covalency by the inclusion of the a^4 term.

However, one can assess the extreme possibility of central field covalency alone by setting $a^4 = 1$ and finding z_{eff} from an empirical expression of the form $B_{\text{free ion}} = \text{const.} \times (z_{\text{eff}} + Z)$, or by solution of the Jørgensen—Racah (or a similar) equation for z, knowing B_{obsd}. Alternatively the possibility of all symmetry restricted covalency may be treated by assuming $z_{\text{eff}} = z$, so that the coefficient of presence of the metal orbital, a^2, is given to a reasonable approximation simply by $\beta^{\frac{1}{2}}$. The more usually adopted course though has been to follow Jørgensen in assuming the two contributions to be of comparable importance and to assign $\beta^{\frac{1}{2}}$ to each effect. Thus one obtains $\alpha^2 = \beta^{\frac{1}{4}}$ and derives z_{eff} using $B = B_{\mathrm{free\ ion}} \cdot \beta^{\frac{1}{2}}$. The values of z_{eff} and α^2 obtained by assuming the extreme behaviour of all central field or all symmetry restricted covalency are denoted by z_{min} or α^2_{min}, whilst those derived by assigning $\beta^{\frac{1}{2}}$ to each effect we denote by z_{root} respectively. Thus in Tables 1—3 we collect together the data for the 3*d*, 4*d* and 5*d* series: in the Tables we show two sets of z_{min} and z_{root} values derived in one case from the Jørgensen—Racah relationship and in the other by using the Slater—Condon parameters obtained from atomic spectra by Oleari and co-workers.

Nevertheless, however useful these procedures may prove in assessing the extent of metal—ligand interaction they are by no means immune to criticism. Thus the assumed α^4 dependence of B_{complex} will become increasingly less valid as the extent of ligand mixing becomes greater, simply because contributions from the ligand and from mixed ligand—metal distributions are tacitly ignored. The derived value of α^4 will therefore be too great and the extent of covalency will be underestimated. Unfortunately, any corrections aimed at rectifying this fault would require knowledge of a large number of repulsion integrals which are only available by molecular orbital calculations, and would have to be evaluated for each individual complex in any case. Since this is clearly an impractical way of treating empirical data it is fortu-

TABLE 1

Interpretations of the nephelauxetic effect in the 3*d* series

Complex	B_{35} (cm^{-1})	β_{35}	z_{min}	α^2_{min}	z_{root}	α^2_{root}	z_{min} [a]	z_{root} [a]	Dq (cm^{-1})
VF_6^{3-}	670	0.78	1.5	0.88	2.1	0.94	1.30	2.05	1610
CrF_6^{3-}	735	0.80	1.5	0.89	2.1	0.95	1.15	1.95	1520
MnF_6^{3-}	782	0.80	1.4	0.89	2.05	0.95	0.70	1.75	1740
FeF_6^{3-}	800	0.77	1.2	0.88	1.9	0.94	—0.35	1.25	1300
CoF_6^{3-}	765	0.70	0.7	0.84	1.55	0.91	[b]	0.20	1410
NiF_6^{3-}	703	0.61	0.3	0.78	1.1	0.88	[b]	0.00	1620
CuF_6^{3-}	641	0.53	—0.1	0.73	0.7	0.85	[b]	—1.00	1410
CrF_6^{2-}	608	0.57	0.7	0.75	1.65	0.87	[b]	1.75	2200
MnF_6^{2-}	585	0.55	0.55	0.74	1.5	0.86	[b]	0.80	2220
CoF_6^{2-}	635	0.53	0.35	0.73	1.2	0.85	[b]	—0.40	2030
NiF_6^{2-}	515	0.41	—0.1	0.64	0.65	0.80	[b]	[b]	2010

[a] Values derived from Slater—Condon parameters of Oleari and co-workers; other z values derived via the Jørgensen—Racah relationship.

[b] z value too negative to be estimated.

TABLE 2

Interpretations of the nephelauxetic effect in the 4*d* series

Complex	B (cm^{-1})	β	$z_{\min}$	$a^2_{\min}$	z_{root}	a^2_{root}	$z_{\min}$ [a]	z_{root} [a]	Dq (cm^{-1})
MoF_6^{3-}	570	0.90	2.05	0.95	2.35	0.97	1.90	2.45	2350
RuF_6^{3-}	550	0.80	1.25	0.89	1.9	0.95	−0.85	0.45	2200
RhF_6^{3-}	460	0.64	0.6	0.80	1.2	0.89	[b]	[b]	2230
AgF_6^{3-}	472	0.61	0.4	0.78	1.0	0.88	[b]	[b]	1840
TcF_6^{2-}	530	0.75	1.35	0.87	2.25	0.93	0.0	1.55	2840
RuF_6^{2-}	500	0.68	0.9	0.82	1.8	0.91	[b]	0.25	2500
RhF_6^{2-}	410	0.54	0.4	0.73	1.1	0.86	[b]	[b]	2050
PdF_6^{2-}	400	0.43	0.1	0.66	0.7	0.81	[b]	[b]	2600
TcF_6^{-}	520	0.70	1.2	0.84	2.4	0.91	−0.15	1.70	2500
RuF_6^{-}	425	0.55	0.6	0.74	1.45	0.86	[b]	−0.40	2600

For footnotes see Table 1.

nate that the errors compounded by the a^4 assumption do not appear to be too serious; thus, for a series of MF_6^{3-} anions of the 3*d* series, with β values lying between 0.6 and 0.9, Fenske et al. [18] showed by SCF—MO calculations that the effect of correcting for the ligand contributions did not alter the calculated β values by more than a few per cent. However, it is clear that for complexes of metals in very high formal oxidation states, which frequently

TABLE 3

Interpretations of the nephelauxetic effect in the 5*d* series

Complex	B (cm^{-1})	ζ (cm^{-1})	β	β^*	$z_{\min}$	$a^2_{\min}$	z_{root}	a^2_{root}	Dq (cm^{-1})
ReF_6^{2-}	543 [a]	2250	0.85	0.77	2.3	0.92	2.95	0.96	3280
OsF_6^{2-}	500 [a]	2900	0.74	0.75	1.35	0.86	2.4	0.93	2600
IrF_6^{2-}	510	3300	0.72	0.73	1.1	0.85	2.2	0.92	2700
PtF_6^{2-}	380	—	0.53	—	0.3	0.73	1.15	0.85	3300
OsF_6^{-}	410 [a]	3200	0.56	0.71	0.55	0.75	1.9	0.87	3500
IrF_6^{-}	360 [a]	3400	0.47	0.66	0.1	0.69	1.3	0.83	2850
OsF_6	310 [a]	3400	0.40	0.64	0.1	0.63	1.25	0.80	—
IrF_6	305 [a]	3400	0.38	0.57	0.0	0.62	1.0	0.79	—
PtF_6	300 [a]	3400	0.36	0.47	−0.1	0.60	0.7	0.77	—

[a] Values essentially B_{55} quantities.

show very small β values, the assumption of the a^4 dependence of B_{complex} must be treated with some caution.

Furthermore, the simplifying assumption by which $\beta^{\frac{1}{2}}$ is assigned to central field covalency, and the same amount to the symmetry restricted effect, is by no means secure. Thus the concept of central field covalency was originally inspired by the diminution of the electrostatic repulsion parameters observed on passing from Mn^{2+}(g) $3d^5$ to Mn^0(g) $3d^5 4s^2$, it being reasoned that the effect of the addition of the two electrons into the 4*s* shell was to some extent a process comparable with the invasion of the outer regions of the partly filled *d*-shell by the electrons of the ligands in a complex. Based on the ^6S—^4G term intervals the β value for Mn^0 $3d^5 4s^2$, with respect to Mn^{2+} $3d^5$, is 0.94, which corresponds to a z_{eff} of 1.75 [16], thus clearly indicating that z_{eff} does not in any way correspond to the actual charge on the metal atom, but merely reflects the situation as regards the repulsion parameters for the partly filled *d*-shell. Of more particular relevance though is the fact that the central field effect produced by the two 4*s* electrons is relatively small, reducing β only from unity to 0.94 and representing an effective screening of only 0.125 units each. Consequently it is difficult to believe that the very low β values observed for some hexafluoride complexes — notably the M^{VI}, MF_6 species of the 5*d* series — can owe as much to central field as to symmetry restricted contributions. The results given in the Tables therefore will most probably underestimate the extent of symmetry restricted covalency, i.e. the listed values of a^2 will be too large.

Many of the problems associated with the attempts to separate central field and symmetry effects are exacerbated though by the theoretical framework in which one is constrained to work. Thus although the molecular orbital description of octahedral transition metal complexes is universally accepted, the concept of the nephelauxetic effect is based upon an essentially ionic model, in which covalency is comprehended only by the departure of the repulsion parameters from their free ion values. Such a comparison is of course necessitated by the need to consider in the ionic model the same orbital occupation number, *n*, for the relevant d^n configuration, as for the occupied, mainly metal *d*-orbitals, of the molecular orbital description. Thus for example for CrF_6^{3-} in the molecular orbital scheme the occupation number of the mainly Cr *d*-orbital t_{2g} level is 3, and hence to consider an analogous configuration one must assess nephelauxetic effects with respect to the Cr^{3+} ($3d^3$) ion. In a molecular orbital approach of course one is not so restricted, and might well choose a basis set which utilised Cr^0 or Cr^+ wave functions, or indeed attempt to use some sort of variable electronegativity or self-consistent charge approach to determine the basis orbitals for the system. Consequently, in applying the nephelauxetic model one is perforce trying to assess the extent of covalency — or more accurately metal—ligand mixing — in what is almost certainly a basis set which constitutes a poor approximation to the actual situation, i.e. one is employing throughout an ionic basis set to describe situations in which the extent of metal—ligand mixing may range from minimal to very large. Clearly the coefficient of presence of the metal orbital, a^2, will have some semi-quantitative significance, even in a poor basis set, but the interpretation of the derived z_{eff} values is more doubtful. Obviously they are meaningful strictly only in an ionic model, but it is perhaps permissible to regard them in an MO scheme as reflecting some sort of variable electronegativity parameter, indicative of an appropriate valence state for the metal basis orbitals.

Quite apart though from the uncertainties discussed above the interpretation of the derived z_{eff} values is, as has been noted earlier, dependent on the fact that they provide only an effective charge for reflecting the value of the electrostatic repulsion parameter. They do not constitute a measure of the actual charge on the metal atom, nor necessarily can they be used to correlate the values of other z dependent physical quantities such as the spin-orbit coupling constant. This latter follows because of the markedly different distance dependence of the contributions to the F_k integrals and to ζ; the former is dominantly an outer orbital function, with an $\langle r^{-1}\rangle$ variation, but the latter is markedly an inner orbital quantity with an $\langle r^{-3}\rangle$ proportionality. Consequently the combination of expressions relating the nephelauxetic and relativistic ratios to a^2 and some function of z_{eff} in order to define both the latter two parameters is probably rather a dubious enterprise, and therefore we do not discuss such results further here. Finally it should be noted that other measures of the effective z value may also be expected not to coincide with those deduced from B_{complex} results.

In principle a z value may be deduced from chemical shifts measured by X-ray photoelectron spectroscopy [19,20]. Where studies have been undertaken such shifts and measurements of the multiplet splitting in the penultimate s shell for compounds of first row transition metals [21] indicate a qualitative agreement with the nephelauxetic parameter. Moreover, although multiplet splitting of the $2p$ photoelectron lines in these compounds is a much smaller effect, differences in the $2p_{\frac{1}{2}}$—$2p_{\frac{3}{2}}$ energy separation have also been shown to depend on the degree of spin delocalisation, thus paralleling the trend in covalency predicted by a consideration of the appropriate β values [22]. To the first order however the $2p_{\frac{1}{2}}$—$2p_{\frac{3}{2}}$ splitting is equal to $\frac{3}{2}\zeta_{2p}$ where ζ_{2p} is the spin-orbit coupling constant for the $2p$ level of the atom involved. This is even more of an inner orbital quantity than ζ_{3d} for example, and as such, excluding multiplet splitting effects, would be expected to be unaffected by covalency. Results obtained from a series of Cr complexes in which the formal oxidation state varies from 0 to 6 support this view [22], but it would be interesting to investigate the corresponding $3p$ and $3d$ doublet separation in similar systems. Unfortunately, however, the resolution at present obtainable with X-ray photoelectron spectrometers, coupled with the relatively small magnitudes of ζ in the outer regions of the atom, precludes such a study.

The results shown in Tables 1—3 reveal a number of interesting features in addition to the trends in the Dq values previously remarked upon. Thus the general tendency throughout is for β values to decrease towards the end of a given transition series, thus reflecting an increasing tendency to covalency and a decreasing stability of the higher oxidation states. In addition, for a given nd^x configuration, of fixed oxidation state, the β values generally increase on passing from the $3d$ to the $4d$ to the $5d$ series, this time reflecting the well known tendency for the higher oxidation states to become more stable in the second and third transition series. In all cases, though, for which data for more than one oxidation state of a given element are available the β values decrease with increasing oxidation number, thus paralleling the increasing metal—ligand mixing. It is noteworthy that in such cases the values of z_{eff} usually show a noticeable decrease with increasing oxidation number, that is the ionic description becomes less appropriate with increase in the formal cationic charge.

Overall therefore, because of the very extensive number of hexafluoro complexes which have been prepared and for which data are to hand the tabulated results provide one of the most comprehensive surveys available of metal—ligand mixing tendencies and oxidation state stabilities for the three d-block transition series. However, although the a^2 parameters clearly have some semi-quantitative significance, the z_{eff} values are manifestly an artifact of the reference B parameters adopted, and can serve only to assess trends in the value of the effective charge on the metal.

(ii) The relativistic ratio, β^*

In principle a knowledge of the relativistic ratio, β^*, for any given complex should be of considerable assistance in assessing the extent of metal—ligand mixing. In practice, though, the situation is less accommodating. Thus, in order to be able to determine ζ from the electronic spectra with any reasonable accuracy one requires that this quantity should be of the order of 2000 cm^{-1} or more, a condition which is only fulfilled in the third transition series. However, although the free ion values of ζ are well established, even for some of the higher oxidation states, in the $3d$ and $4d$ series, such data are sparse or lacking altogether for the $5d$ elements. Consequently, for the M^{IV}, M^{V} and M^{VI} species of that series one is forced to obtain the free ion values by various, and somewhat dubious, extrapolation or interpolation techniques, with the result that the values used are probably not reliable to much better than about ±15%. The usefulness of the deduced β^* values is therefore appreciably reduced, although they are still of utility in conjunction with the β values, and for assessing changes in covalency tendencies within a series of related complexes, for example the hexahalo anions of Os^{IV} and Ir^{IV} [7].

Bearing in mind these limitations we can proceed by assuming with Jørgensen [16] that whereas for a given complex the repulsion parameter, B, is proportional to $a^4(z_{eff} + Z)$, the spin-orbit coupling varies with $a^2(z_{eff} + Z)^2$, where z_{eff} and Z are as previously defined. Once again some error is occasioned by the neglect of the ligand contributions, but here we are dealing with a one electron operator, and moreover the spin-orbit coupling constant for F^- is only some 220 cm^{-1} as compared with values of the order of 3,000 cm^{-1} for the 5*d* metals. We have previously reviewed [5] the various ways in which estimates of the value of a^2 and of the extent of central field covalency may be obtained from the β^* values. Suffice it to say that we have grave misgivings about attempts to obtain values of both a^2 and z_{eff} (or some related quantity) by combining β and β^* data with the assumption of a fixed z_{eff}. This is because as noted before B is an outer orbital function with a $\langle r^{-1}\rangle$ dependence, and ζ an inner orbital quantity with a $\langle r^{-3}\rangle$ dependence. Consequently the same value of z_{eff} cannot be expected to reproduce in both cases the effect of involvement of the metal in complex formation. It seems probable though that were accurate reliable values of β^* to be available these would constitute a tolerable estimate for a^2 in hexafluoro species; thus for the higher oxidation states in the 5*d* series, for which a^2_{min} is probably a better estimate than a^2_{root}, values of β^* do begin to approach those of a^2_{min}. In fact the assumption that β^* approximates to a^2 is equivalent to dismissing the effect of central field covalency on the spin-orbit coupling constant. Conceptually though this is not at all unreasonable. The central field effect on B is conceived as arising from the invasion by the ligand electrons of the outer orbital regions constituted by the partially filled *d*-shell, and such a process would be expected to have little influence on the magnitude of an $\langle r^{-3}\rangle$ dependent quantity: the only way in which ζ should be substantially changed is by actual metal—ligand mixing, with a consequent reduction in the coefficient of presence, a^2, of the metal in the corresponding molecular orbital. Furthermore, support for this interpretation is forthcoming from theoretical studies, since Al-Mobarak and Warren [23] showed that even for the 3*d* series more than 90% of the total value of ζ_{3d} arose from the region within 1 a.u. of the nucleus, well inside the region of effectual metal—ligand overlap, so that the effect of central field contributions on the outer regions of the *d*-orbital should be negligible. For the 5*d* series no suitable analytical wave functions were available, but because of the approximate Z^4 dependence of ζ the situation in the 5*d* series should be even less propitious for the operation of central field effects.

Thus, in Table 3, because of the uncertainties both in β^* and in regard to its proper interpretation, we have simply listed the β^* values where appropriate, and without further comment. Finally it is perhaps pertinent to point out that the uncertainty in the derived value of $\zeta_{complex}$ does vary according to the $5d^n$ configuration under investigation: thus for d^4 and d^5 systems the spin—orbit splitting of the ground state approximates to $\frac{3}{2}\zeta$, and is directly observable optically, but for d^3 and d^6 systems the ground states are unsplit by spin—orbit coupling. For d^3 systems ζ is derived primarily from the splitting of the ${}^4A_{2g} \rightarrow {}^2T_{2g}$ band, but for d^6 complexes only a rough estimate for ζ may be deduced using the relative intensities of the formally spin-forbidden and spin-allowed bands. For d^1 and d^2 systems, e.g. ReF_6 and OsF_6, the spin—orbit splitting of the ground state again equals $\frac{3}{2}\zeta$ to the first order, and is directly detectable [24].

C. CHARGE-TRANSFER BANDS AND OPTICAL ELECTRONEGATIVITIES

In Fig. 1 we show the qualitative molecular orbital scheme appropriate for the description of octahedral transition metal hexahalo complexes. The ligand σ-orbitals give rise to the symmetry adapted combinations $a_{1g} + e_g + t_{1u}$, and the π-orbitals to the levels $t_{1g} + t_{2g} + t_{1u} + t_{2u}$, and for a formally d^n complex the occupied levels in the ground state correspond to dominantly ligand levels up to and including t_{1g}, followed by n electrons in the predominantly metal t_{2g} and e_g levels. For the 4d and 5d series the ground states are always low-spin systems, but in the 3d series, although the MF_6^{2-} species all show low-spin behaviour, the MF_6^{3-} complexes are high-spin with the exception of NiF_6^{3-}.

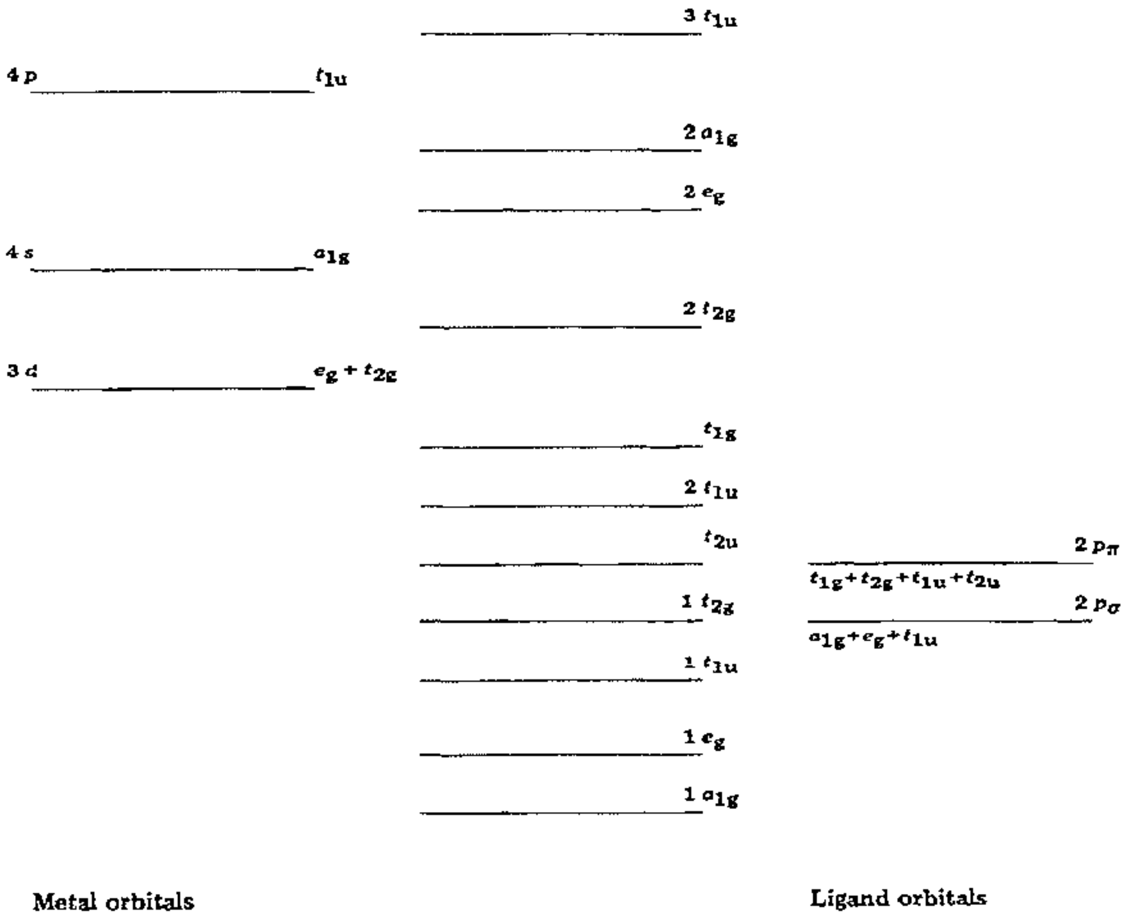

Fig. 1. Molecular orbital scheme for octahedral hexafluoro complexes.

Whilst the ordering of the mainly metal levels is not in doubt, that of the predominantly ligand levels is still subject to some uncertainty. However, those derived from π-type ligand orbitals lie appreciably higher than those originating from σ-orbitals, and recent studies of charge-transfer bands for 5*d* systems, using MCD techniques [25], suggest the energetic ordering $\pi t_{1g} > (\pi + \sigma)t_{1u} > \pi t_{2u} \sim \pi t_{2g} > (\sigma + \pi)t_{1u}$. Clearly therefore the lowest energy charge-transfer bands should correspond to $\pi \rightarrow t_{2g}$ type transitions, or to $\pi \rightarrow e_g$ transitions for systems in which the t_{2g} shell is fully occupied in the ground state. It is clear that ligand to metal charge-transfer transitions which correspond to u → g excitations will constitute formally allowed electronic transitions in contrast to the *d*—*d* bands which derive their intensity by vibronic interactions. Consequently such charge-transfer bands would be expected to be significantly more intense than the *d*—*d* bands, and for those species for which solution measurements are possible this prediction is fully realised. However, as explained elsewhere, for diffuse reflectance spectra it is not possible to derive satisfactory estimates of intensities, although it is generally possible to assign the beginning of the charge-transfer region of the spectrum without ambiguity. Moreover, even for solution spectra it is often difficult to assign the whole of the charge-transfer region of the spectrum because of the breadth of the bands concerned, and consequently we here direct our attention primarily towards the examination of the positions of the first charge-transfer bands which will usually correspond to the $(\pi + \sigma)t_{1u} \rightarrow t_{2g}$ (or e_g) transition.

Much of our present understanding of charge-transfer transitions in hexahalo species is due to the early solution measurements of Jørgensen [26] on the hexachloro, hexabromo and hexaiodo anions of the 4*d* and 5*d* series, on the basis of which were postulated the relationships

$$(\pi \rightarrow t_{2g}) = V + kD + q(A - E) \tag{1}$$

and

$$(\pi \rightarrow e_g) = V + k'D + q(A - E) + \Delta \tag{2}$$

for complexes formally possessing d^q configuration. More recently it was shown that these relationships are valid for the hexafluoro species of the 4*d* and 5*d* series, and also for the hexafluoro anions of the 3*d* series. Here V is a parameter depending on the nature of the ligand, the oxidation state of the metal, and the particular series, and D is the spin-pairing energy. E contains the variation of the orbital energy of the t_{2g} (or e_g) electrons with the occupation number, q, and A is approximately equal to the corresponding Racah parameter. The values of the spin-pairing contributions for a given metal ion configuration are given by $-S(S + 1)D$, where S is the total spin, and from this the values of k and k' for the various d^q systems may readily be found and have been tabulated by Allen et al. [6].

In Tables 4 and 5 therefore we show the values of the V, D and $(E - A)$ parameters obtained for the MF_6^{2-} and MF_6^{3-} complexes of the 3*d* and 4*d*

TABLE 4

Calculated positions of charge-transfer bands in MF_6^{n-} species of the 3*d* series

	Transition	Obsd. (kK)	Calcd. (kK)
MF_6^{3-} Anions			
TiF_6^{3-}	$\pi \rightarrow t_{2g}$	48	48
VF_6^{3-}	$\pi \rightarrow t_{2g}$	43	40
CrF_6^{3-}	$\pi \rightarrow t_{2g}$	55—60	54
MnF_6^{3-}	$\pi \rightarrow t_{2g}$	50—55	53
FeF_6^{3-}	$\pi \rightarrow t_{2g}$	49	51
CoF_6^{3-}	$\pi \rightarrow t_{2g}$	41	42
NiF_6^{3-}	$\pi \rightarrow e_g$	32	31
CuF_6^{3-}	$\pi \rightarrow e_g$	30	36
$V = 60.0$, $(E - A) = 5.5$, $D = 6.0$ kK			
MF_6^{2-} Anions			
VF_6^{2-}	$\pi \rightarrow t_{2g}$	34	37
CrF_6^{2-}	$\pi \rightarrow t_{2g}$	30	30
MnF_6^{2-}	$\pi \rightarrow t_{2g}$	39	44
CoF_6^{2-}	$\pi \rightarrow t_{2g}$	28	30
NiF_6^{2-}	$\pi \rightarrow e_g$	31	37
$V = 48.5$, $(E - A) = 4.5$, $D = 5.5$ kK			

series, together with a listing of the observed and calculated band positions. In a number of cases in the 4*d* series the first charge-transfer band lies above the accessible region of the spectrum, but in those instances a good estimate of the band energy for the MF_6^{n-} species can be derived by adding 26 kK (equivalent to the optical electronegativity difference) to the corresponding value for the MCl_6^{n-} system. For both the 3*d* and the 4*d* series the data for the MF_6^{2-} anions are well correlated by the expressions given, but the agreement between the observed and calculated band positions is less satisfactory for the MF_6^{3-} ions, particularly towards the end of the series. This is probably due to the fact that whereas the MF_6^{2-} data relate only to species with t_{2g}^p ground state configurations, some of the MF_6^{3-} results refer to anions in which the e_g level is partially occupied [27]. We are therefore dealing with $(E - A)$ quantities for e_g as well as for t_{2g} orbitals, the former probably being somewhat greater in magnitude. The data for the MF_6^{3-} complexes were therefore interpreted by omitting the data for CuF_6^{3-} and AgF_6^{3-} respectively when deriving the V, D and $(E - A)$ parameters. In all cases the values of D are strictly speaking not constant within a given series, being equal to $\frac{7}{6} \times (\frac{5}{2}B + C)$ theoretically, but in practice the D values calculat-

TABLE 5

Calculated positions of charge-transfer bands in MF_6^{n-} species of the 4*d* series

	Transition	Obsd. (kK)	Calcd. (kK)
MF_6^{3-} Anions			
MoF_6^{3-}	$\pi \rightarrow t_{2g}$	71 [a]	71
RuF_6^{3-}	$\pi \rightarrow t_{2g}$	55	55
RhF_6^{3-}	$\pi \rightarrow t_{2g}$	65 [a]	65
AgF_6^{3-}	$\pi \rightarrow e_g$	28	57
$V = 82.0$, $(E-A) = 6$, $D = 4.0$ kK[b]			
MF_6^{2-} Anions			
TcF_6^{2-}	$\pi \rightarrow t_{2g}$	55 [a]	56
RuF_6^{2-}	$\pi \rightarrow t_{2g}$	48	48
RhF_6^{2-}	$\pi \rightarrow t_{2g}$	40	41
PdF_6^{2-}	$\pi \rightarrow e_g$	55 [a]	56
$V = 63$, $(E-A) = 5$, $D = 4$ kK			

[a] Values derived from data for corresponding MCl_6^{n-} species.
[b] Fitted without AgF_6^{3-} result.

ed from the B_{obs} results show very little spread within a given sequence. Consequently there is no sensible error involved in assuming D to be constant, but for further details the reader is referred to our previous surveys [4,5].

However, in whichever way the parameter D is determined its use in conjunction with the position of the first ligand—metal charge-transfer band permits the evaluation of Jørgensen's optical electronegativity parameters. These are derived via the relationship

$$\sigma_{corr} = (\chi_{opt}(X) - \chi_{opt}(M^{n+})) \times 30 \text{ kK}$$

where $\chi_{opt}(X)$ is the optical electronegativity of the ligand and $\chi_{opt}(M^{n+})$ that of the metal cation corresponding to the oxidation state of the complex. For F^- χ_{opt} is 3.9 on the Pauling scale.

Two corrections are normally applied to the observed band position of the lowest energy charge-transfer transition. Firstly, $\pi \rightarrow e_g$ and $\pi \rightarrow t_{2g}$ transitions are compared directly by subtracting Δ (10 Dq) from the former, and secondly corrections are applied to compensate for the change in the spin-pairing energy relating to the metal orbitals which accompanies the $d^q \rightarrow d^{q+1}$ transition. These quantities have been explicitly listed, and their derivation discussed before [4—6].

The values of χ_{opt} thus obtained show two interesting correlations. In the

TABLE 6

Optical electronegativities for oxidation states of the 3*d* series

Element	M^{III}	M^{IV}
Ti	2.2	—
V	2.25	2.6
Cr	2.4	2.65
Mn	2.65	3.05
Fe	2.9	—
Co	3.0	3.1
Ni	3.05	3.4
Cu	3.24	—
Slope χ_{opt} vs. q (kK)	5.0	4.3

first place χ_{opt} for a given M^{n+} state affords a measure of the facility with which an electron is transferred from the ligand to the metal, and strongly oxidising states show charge-transfer bands at low energies and yield high χ_{opt} values. Since the nephelauxetic ratio, β, also assesses the extent of electron accession to the metal, or metal—ligand mixing, one would not be surprised to find a parallel between χ_{opt} and β, and this expectation is fulfilled in the experimental results as shown in Tables 6 and 7. Of course χ_{opt} is in principle independent of the nature of the ligand, so that a correlation should only subsist when β values are considered for a constant halide ligand. With these limitations the problem has been considered on a theoretical basis by Allen and Warren [28], and a justification of the relationship on a semi-quantitative basis derived.

TABLE 7

Optical electronegativities for oxidation states of the 4*d* series

Element	M^{III}	M^{IV}	M^{V}
Mo	1.7	1.9	2.05
Tc	—	2.2	2.4
Ru	2.15	2.5	2.8
Rh	2.3	2.65	—
Pd	—	2.7	—
Ag	3.3	—	—
Slope χ_{opt} vs. q (kK)	9.5 (6.2) [a]	5.3	12.0

[a] Excluding Ag^{III}.

In addition, Jørgensen [29] has shown that a roughly linear relationship should hold between χ_{opt} and the *d*-orbital occupation number, q, for a given oxidation state, and that the slope of the χ_{opt} vs. q plot should approximately equal $(E - A)$. For the hexafluoro species of the 3*d* and 4*d* series the data of Tables 4—7 show that both of these predictions are satisfactorily fulfilled.

We have however postponed until now the treatment of the charge-transfer data relating to the 5*d* series, since their treatment requires an extension of the theoretical framework outlined above. In particular, in the 5*d* series, the spin-orbit coupling constant is markedly larger than in the 3*d* or 4*d* series, and some of the resulting splittings become comparable in magnitude to the term separations resulting from the electrostatic repulsion operator. Consequently the changes in the ζ terms which may accompany a given $d^q \rightarrow d^{q+1}$ charge-transfer transition will be of similar magnitude to the changes in the

TABLE 8

Calculated positions of charge-transfer bands for MF_6^{z-} species of the 5*d* series

	Transition	Obsd. (kK)	Calcd. (kK)
MF_6^{2-} Anions			
ReF_6^{2-}	$\pi \rightarrow t_{2g}$	57*	57
OsF_6^{2-}	$\pi \rightarrow t_{2g}$	55	56
IrF_6^{2-}	$\pi \rightarrow t_{2g}$	48	45
PtF_6^{2-}	$\pi \rightarrow e_g$	64*	67
$V = 79$, $(E-A) = 8.0$, $D = 4.5$, $\zeta = 3$ kK			
MF_6^- Anions			
ReF_6^-	$\pi \rightarrow t_{2g}$	$\nless 40$	49
OsF_6^-	$\pi \rightarrow t_{2g}$	42	42
IrF_6^-	$\pi \rightarrow t_{2g}$	42	41
PtF_6^-	$\pi \rightarrow t_{2g}$	29	31
$V = 68$, $(E-A) = 8.5$, $D = 3.0$, $\zeta = 3$ kK			
MF_6 Species			
WF_6	$\pi \rightarrow t_{2g}$	57	55
ReF_6	$\pi \rightarrow t_{2g}$	48	44
OsF_6	$\pi \rightarrow t_{2g}$	36	38
IrF_6	$\pi \rightarrow t_{2g}$	28	28
PtF_6	$\pi \rightarrow t_{2g}$	25	26
$V = 58$, $(E-A) = 9.5$, $D = 2.5$, $\zeta = 3$ kK			

spin-pairing energy, and correction should therefore also be made to the value of σ_{obs} in order to compensate for these effects too. Thus, one of us [30] has shown that in the 5*d* series the situation approximates fairly well to *jj* coupling in which the interaction matrices are diagonal in ζ, and proceeding on this basis, using the $p^n - t_{2g}^{6-n}$ isomorphism, the corrections which must be applied to σ_{obs} (and in a contrary sense to eqns. 1 and 2) are readily derived. In this way the results shown in Table 8 were derived, via eqns. 1 and 2, and once again good agreement is obtained between the experimental and calculated band positions. (Note that in order to distinguish optical electronegativity values which include spin-orbit corrections from those that do not the suffix * is appended to the former).

As shown in Table 9 the use of the χ_{opt}^* quantities for the 5*d* series also leads to a good correlation being obtained between χ_{opt}^* and β, as in the 3*d* and 4*d* series, as well as satisfactory linear plots for χ_{opt}^* vs. q, the orbital occupation number. Once again the data given in the Tables are entirely consistent, and the $(E - A)$ results obtained from χ_{opt}^* vs. q agree closely with those deduced via eqns. 1 and 2.

Overall therefore the charge-transfer data for the three transition series may all be satisfactorily interpreted in terms of the spin-pairing energy and optical electronegativity concepts, as long as corrections are applied where spin-orbit effects are significant. Because of the parallel established between χ_{opt} and β the values of the former parameter also afford some measure of the metal—ligand mixing tendencies as well as assessing the ease or difficulty of electron donation to the metal. We therefore conclude that a study of the electronic spectra of the hexafluoro species of the transition metals can yield useful information about the extent of metal—ligand mixing, via β, and about the stabilities of metals in various oxidation states, via χ_{opt}, but that the information content of the β^* values is rather limited because of the experimental uncertainties involved, and that little absolute value can be placed upon the various z_{eff} values derived.

TABLE 9

Spin—orbit corrected optical electronegativities for oxidation states of the 5*d* series

Element	M^{IV}	M^{V}	M^{VI}
W	1.85	1.9	1.95
Re	2.05	$\ngtr 2.5$	2.15
Os	2.35	2.5	2.7
Ir	2.5	2.75	2.95
Pt	2.65	3.15	3.3
χ_{opt}^* vs. q slope (kK)	6.6	8.9	10.0

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