Comparative Interpretation of Absorption Spectra of Tc(IV) and Rhenium (IV) Hexahalides

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Fig. 1. Absorption spectra of technetium (IV) hexahalides.

Fig. 2. Absorption spectra of rhenium (IV) hexahalides.
Table 1. Absorption bands of technetium(IV) and rhenium(IV) hexahalides. Shoulders are given in parentheses.

The assignments of the excited levels are discussed in the text.
$2^1T_3$ and $2^1T_4$ (which are nearly coincident if the $\gamma_5$ orbitals have angular functions characterizing $l = 2$) and $2^1T_5$. If the relativistic effects are predominant, i.e. the Landé parameter $\zeta_{\text{nd}}$ of the central atom is large, as is the case for Re, a weak splitting into five excited components is predicted.

(2) Broad but relatively weak bands, caused by the spin-allowed transitions to the two levels $4^2T_5^0$ and $a^2^2T_4$ belonging to the excited sub-shell configuration $\gamma_5^3\gamma_3$. Because a weakly $\pi$-anti-bonding $\gamma_5$ electron is transferred to the highly $\sigma$-anti-bonding $\gamma_3$ orbital, the internuclear distances at equilibrium of the excited electronic state are increased and the Franck-Condon principle demands co-excitation of a wide vibrational structure. However, at least at room temperature and in solution, this structure is always blurred out, and only a Gaussian error-curve shaped band results. These bands are only observed with certainty in TcF$_6$ and ReF$_6$; in our six other species, they are covered by the much stronger bands of class (3).

(3) Intense bands caused by electron transfer from orbitals (six $\sigma$ and twelve $\pi$) on the ligands to the partly filled shell. The lowest excited configuration type is $\sigma^{12}\pi^{22}\gamma_5^3\gamma_3^4$ whereas configurations such as $\sigma^{12}\pi^{23}\gamma_5^3\gamma_3^3$ or $\sigma^{11}\pi^{24}\gamma_5^3\gamma_3^3$ have higher energy. It is possible to apply molecular orbital (M.O.) theory to these electron transfer spectra with the same success as to the “ligand field” transitions in the partly filled shell, and it is again necessary to take certain relativistic effects into account in bromide and iodide complexes where the ligands have a large value of $\zeta_{\text{mp}}$. Since the internuclear distances at the minimum of the potential surfaces belonging to the configurations $\sigma^{12}\pi^{24}\gamma_5^3$ and $\sigma^{12}\pi^{23}\gamma_5^3\gamma_3^4$ do not seem very different, the first electron transfer bands can be relatively narrow.

**Intra-sub-shell Transitions**

Perhaps the most striking regularity of the spectra obtained is the shift of wavenumbers:

$$
\begin{align*}
\text{ReI}_6^- &< \text{ReBr}_6^- < \text{ReCl}_6^- < \text{ReF}_6^- \\
\text{TcI}_6^- &< \text{TcBr}_6^- < \text{TcCl}_6^- < \text{TcF}_6^- 
\end{align*}
$$

for the narrow, weak band of class (1) as well as the strong electron transfer bands (3). However, the physical reason is entirely different in the two cases. As we shall see below, the series (1) applies to the electron transfer bands because of the varying one-electron energy of the ligand $\pi$-orbitals; iodide is more reducing than fluoride. On the other hand, the intra-sub-shell transitions obey (1) because they express effects of interelectronic repulsion, and the parameters of interelectronic repulsion are under equal circumstances inversely proportional to the average radius of the partly filled shell. The variation of these parameters below the values found in the corresponding gaseous ions (here Tc$^{4+}$ and Re$^{4+}$) is called the nephelauxetic effect, i.e. the cloud-expanding of the d-shell participating in the formation of $\sigma$-anti-bonding M.O. and also adapted to a lower effective charge of the central atom because of partly covalent bonding of the other orbitals. Actually, the energy differences 10 000 cm$^{-1}$ to 20 000 cm$^{-1}$ occurring in the half-filled sub-shell $\gamma_5^3$ are ideal examples of the general situation, not very familiar to many chemists that the energy of such a molecule cannot be evaluated from the knowledge of the electronic density in our three-dimensional space alone, but that one has to know as well the second-order density matrices or operators in a six-dimensional space. This, of course, is still a considerable simplification relative to a conventional wavefunction needing three spatial variables per electron participating. Said in other words, the various levels of $\gamma_5^3$ have essentially the same average electronic density in our space, but if two electrons are considered at a time, they have in average larger distances between them in the groundstate $4^2T_2$ than in the excited levels.

To the first approximation the energy difference from $4^2T_2$ to $2^1T_3$ and $2^1T_4$ is $3K$ ($4, 5$) and from $4^2T_2$ to $2^1T_5$ is $5K$ ($4, 5$) where the “exchange integral” $K$ ($4, 5$) represents $(3B + C)$ in terms of Racah’s parameters. It is seen from Table 1 that the ratio between the wavenumbers of the two spin-forbidden transitions in Mo(III) and Tc(IV) complexes varies between 1.58 and 1.50. The main

19 M. LINHARD and M. WEIGEL, Z. Anorg. Chem. 266, 49 [1951].
reason for the decrease below the first-order value 1.67 is that $2\Gamma_5$ is somewhat more stabilized by intermixing with the other sub-shell configurations $\gamma_5^2 \gamma_3$ and $\gamma_3^2 \gamma_5$ than $2\Gamma_3$ and $2\Gamma_4$. This discrepancy was first discussed by Tanabe and Sugano. In the Re(IV) and Ir(VI) hexahalides, the relativistic effects are more important, corresponding to a larger value of the Landé parameter $\zeta_{\text{sd}}$ of the central atom, and we denote the separated components with Bethe's double-group quantum numbers, the groundstate $4T_2$ being $a \Gamma_8$, the nearly coincident $2T_3$ and $2T_4$ becoming $b \Gamma_8$, $c \Gamma_8$ and $\Gamma_6$, and $2\Gamma_5$ separating in $\Gamma_7$ and $d \Gamma_8$. If second-order perturbation theory is applied to Eisenstein's determinants, the approximate energy turns out to be, assuming $C = 4B$.

$$a \Gamma_8: -\frac{z^2}{35B} - \frac{3z^2}{5A},$$
$$b \Gamma_8: \frac{21B}{56B} - \frac{k_1B}{A} - \frac{3z^2}{A},$$
$$c \Gamma_8: \frac{21B}{56B} - \frac{k_2B}{A} - \frac{3z^2}{A},$$
$$\Gamma_6: \frac{21B}{24B} - \frac{3z^2}{A},$$
$$\Gamma_7: \frac{35B}{176B} - \frac{3z^2}{A},$$
$$d \Gamma_8: \frac{35B}{280B} + \frac{33z^2}{176B} - \frac{3z^2}{A}.$$

Second-order perturbation theory cannot be directly applied to the levels $b \Gamma_8$ and $c \Gamma_8$. The sum $k_1 + k_2 = 114$ is distributed as $k_1 = 50.4$ and $k_2 = 63.6$ if the diagonal difference between $2T_3$ and $2T_4$ is negligible compared to $z^2/B$. It is remarkable that the second-order perturbation from spin-orbit coupling with the higher sub-shell configuration $\gamma_5^2 \gamma_3$ is the same for all six energy levels of $\gamma_3^3$, viz. $-3z^2/A$, and hence has no influence on the energy differences observed.

Two effects may be remarked which make second-order perturbation theory slightly less suitable than usually: we have made a summation of the squared matrix elements of $B$ and $z$ independently, disregarding their phase relations; and we have neglected the fact, which Dr. W. Schneider, ETH Zürich, was so kind as to point out to us: that nearly all the sub-shell configuration intermixing in $2T_3$ comes from a particularly large non-diagonal element of interelectronic repulsion, i.e. $\sqrt{7}B$ with one of the two $2T_3$ levels of $\gamma_5^2 \gamma_3$, which happens to be as high as $A + 26B$ and not only $A$ above the energy of the unperturbed $2T_3$ of $\gamma_3^3$. Hence, the usual second-order perturbation expression for the energy of $2T_3$, $2B - 90B^2/A$, tends to exaggerate the depression, especially in chromium(III) complexes with low values of $A/B$, by a factor roughly two.

We have a rather indirect way to determine $\zeta_{\text{sd}}$ in our rhenium(IV) complexes and in IrF$_6$ studied by Moffitt, Goodman, Fried and Weinstock to put the observed energy difference between the $\Gamma_7$ and $d \Gamma_8$ components equal to $33z^2/280B$ according to eq. (2). The values obtained,

$$3100 \text{ cm}^{-1} \text{ IrF}_6; \quad 2450 \text{ cm}^{-1} \text{ ReBr}_6^-; \quad 2400 \text{ cm}^{-1} \text{ ReCl}_6^-; \quad \text{and } 2550 \text{ cm}^{-1} \text{ ReF}_6^-$$

are rather uncertain, ±20%. They may be compared to the values $\zeta_{\text{sd}} = 3500 \text{ cm}^{-1}$ for gaseous ReF$_6$, $3400 \text{ cm}^{-1}$ for gaseous OsF$_6$, and $2800 \text{ cm}^{-1}$ for OsCl$_6^-$. Johannesen and Candela proposed another assignment of few of the excited levels of the latter ion (these authors considered that the bands at 10 800 and 11 800 cm$^{-1}$ are caused by trigonal splitting, the cubic energy levels being lower) and suggested $\zeta_{\text{sd}} = 2100 \text{ cm}^{-1}$ for OsCl$_6^-$ and OsBr$_6^-$. It is known from gaseous ions and from the relative intensities of spin-forbidden and spin-allowed transitions in Mo(III) complexes that the order of magnitude expected for $\zeta_{\text{sd}}$ in Tc(IV) complexes is 1000 cm$^{-1}$. Hence, the energy difference $33z^2/280B$ between the components $\Gamma_7$ and $d \Gamma_8$ is expected to be only some 300 cm$^{-1}$ which is on the limit of the experimentally discernible quantities.

Table 2 gives the nephelauxetic ratio $\beta_{35}$ between the value for $7B$ derived for the complexes according to eq. (2) and the values known or extrapolated for the gaseous ions, viz. $7B = 7450 \text{ cm}^{-1}$ for Mn$^{2+}$, $4260 \text{ cm}^{-1}$ for Mo$^{3+}$, $4930 \text{ cm}^{-1}$ for Tc$^{4+}$, $4550 \text{ cm}^{-1}$ for Re$^{4+}$, and $5670 \text{ cm}^{-1}$ for Ir$^{6+}$. In all cases, a moderate nephelauxetic ratio $\beta_{35}$ is observed, the extreme values being 0.47 for the highly covalent IrF$_6$ and 0.83 for the isoelectronic ReF$_6^-$. It is seen that $\beta_{35}$ in average is very slightly smaller, some 0.03, in Tc(IV) than in the corresponding Re(IV) hexahalide. It cannot be safely

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concluded that $\text{MnF}_6^-$ is less nephelauxetic than $\text{TcF}_6^-$; Schenider's phenomenon mentioned above tends to decrease $\beta_{55}$ of Mn(IV) by a few percent. The values of $\Delta$ are in certain cases ($\sim$ signs) extrapolated from well-known properties of the spectrochemical series \(^1\). Actually, the correction factors $(1 - 3B/A)$ and $(1 - 5B/A)$ which can be derived from eq. (2) [$5B/A$ representing $176B^2/(35B/A)$, for instance] only vary between 0.89 and 0.97 in the complexes studied, and they are nearly invariant in the cases of Tc(IV) and Re(IV).

The vibrational structure of the bands in the near infra-red of $\text{ReCl}_6^-$ corresponds to a nearly equidistant progression with the characteristic wavenumber $\sigma_c = 150$ to $200$ cm$^{-1}$, whereas the similar structure \(^8\) of the transition to $\Gamma_1^*$ is equidistant with $\sigma_c = 150$ cm$^{-1}$. The same is true \(^{11}\) for the transition $a \Gamma_1 (\Gamma_4') \rightarrow b \Gamma_1 (\Gamma_1')$ of $\text{OsCl}_6^-$ at $17250$ cm$^{-1}$ with $\sigma_c = 170$ cm$^{-1}$. However, there are good reasons to believe that this regularity is an accident because one of the bending frequencies of $\text{MCl}_6^-$ is rather exactly half one of the stretching frequencies. Thus, the bending even $\Gamma_5$ mode has the vibrational quantum $158$ cm$^{-1}$ in $\text{SnCl}_6^-$ and $162$ cm$^{-1}$ in $\text{PtCl}_6^-$ whereas the totally symmetric stretching even $\Gamma_1$ correspond to $311$ cm$^{-1}$ and $344$ cm$^{-1}$ in these two complexes \(^{28}\). The following frequencies in cm$^{-1}$ are now known from Raman spectra of solution \(^{29}\):

$$\begin{align*}
\text{ReCl}_6^- & : 346, 275, 313, 172, 159; \\
\text{ReBr}_6^- & : 213, 174, 217, 118, 104.
\end{align*}$$

\(^{29}\) L. A. Woodward and M. J. Ware, Spectrochim. Acta \textbf{20}, 711 [1964].

The infra-red absorption spectra, to be discussed in another paper, show lines at:

$$\begin{align*}
K_2\text{TcF}_6^- : 574 \text{ cm}^{-1}; & \quad \text{Rb}_2\text{TcCl}_6^- : 333 \text{ cm}^{-1};; \\
K_2\text{ReF}_6^- : 550 \text{ cm}^{-1}; & \quad \text{Rb}_2\text{ReCl}_6^- : 319 \text{ cm}^{-1}.
\end{align*}$$

\(^{(5)}\) presumably caused by the odd $\Gamma_4$ stretching mode. They may be compared with the lines \(^{30}\) at $294$ cm$^{-1}$ in salts of $\text{SnCl}_6^-$, $300$ and $314$ cm$^{-1}$ for $\text{ReCl}_6^-$, $304$ and $318$ cm$^{-1}$ for $\text{OsCl}_6^-$, $316$ and $324$ cm$^{-1}$ for $\text{IrCl}_6^-$, and $330$ cm$^{-1}$ for $\text{PtCl}_6^-$, whereas the 4$d$ group hexahalides are represented \(^{30}\) by $293$ cm$^{-1}$ for $\text{ZrCl}_6^-$, $332$ cm$^{-1}$ for $\text{RuCl}_6^-$, and $336$ cm$^{-1}$ for $\text{PdCl}_6^-$.

The wavenumbers observed in our fluorides are more than $(35.5/19)^{1/2} = 1.37$ times larger than in the corresponding chlorides. They would suggest that the force constants for $\text{M} - \text{F}$ stretching

are some 50% larger than for M – Cl stretching since the effective reduced mass is known to be closely similar to the ligand mass in this case. They would also suggest, like the results of Adams et al., that the smaller 4d group ions have force constants only some 10% larger than the corresponding 5d group complexes.

The broad doublet structure of $d\Gamma_8$ in ReF$_6$$^-$ (separation 810 cm$^{-1}$), ReCl$_6$$^-$ (480 cm$^{-1}$), and ReBr$_6$$^-$ (340 cm$^{-1}$) probably have another reason than the detailed structure of narrow bands observed in the other intra-sub-shell transitions. There is some evidence that our hexahalides are slightly distorted from regular octahedral symmetry, and that this distortion is more pronounced in the technetium(IV) complexes which might explain the broader bands without much vibrational structure of the latter species. It is realized that the distortions only have minor influence on the absorption spectra, and in particular that the half-filled sub-shell $\gamma_5^3$ is especially stable towards splitting of the energy levels occurring in cubic symmetry. However, this argument is not strictly valid when strong relativistic effects occur, such as in Re(IV) and Ir(VI). Actually, the whole separation might be caused by dynamic Jahn–Teller effect alone. Stephens and Drickamer found that the two components of $d\Gamma_8$ of K$_2$ReCl$_6$ separate strongly, in a reversible way, when the crystals are subject to pressure of some 100,000 atm. This may be ascribed to a distortion of the octahedral ReCl$_6$$^-$, possibly along a threefold axis, to a larger extent than in our solutions.

The weak transitions at 14 200 cm$^{-1}$ and 14 880 cm$^{-1}$ of ReF$_6$$^-$ are probably due to co-excited vibrations similar to those observed for OsCl$_6$$^-$. If their electronic origins are at 10 130 cm$^{-1}$ and 10 890 cm$^{-1}$, respectively, their wavenumbers are 4 000 cm$^{-1}$ which is larger than the O – H stretching frequency of water $\sim$ 3 760 cm$^{-1}$. The broad and extremely weak band $\sim$ 21 300 cm$^{-1}$ of TcF$_6$$^-$ may be due to impurities or to a similar coexcited vibration belonging to the band at 17 610 cm$^{-1}$. ReBr$_6$$^-$ seems to show a co-excited vibration 3 490 cm$^{-1}$ above the “sharpest” previous electronic origin, or 1 860 cm$^{-1}$ above the beginning of $d\Gamma_8$.

**Spin-allowed Transitions**

Analogous to the two transitions to $^4I_5$ and $^4I_4$ observed in the reflection spectrum of K$_2$MnF$_6$ at 21 750 and 28 200 cm$^{-1}$, the two broad bands of TcF$_6$$^-$ at 28 410 and 34 360 cm$^{-1}$ are in perfect agreement with predictions of ligand field theory. The wavenumber of the first transitions represents A, the one-electron energy difference between the two sub-shell $\gamma_5$ and $\gamma_3$, and the distance between the two bands determines Racah’s parameter of interelectronic repulsion B which turns out to be 530 cm$^{-1}$. Since the extrapolated value of B for the isolated Tc$^{+4}$ is 705 cm$^{-1}$, this means that the nephelauxetic ratio $\beta_{35}$ is 0.75, slightly smaller than the value $\beta_{35} = 0.79$. Table 3 compiles values of B and $\beta_{35}$ derived from spin-allowed transitions in TcF$_6$$^-$ and a series of related complexes.

<table>
<thead>
<tr>
<th>Species</th>
<th>A [cm$^{-1}$]</th>
<th>B [cm$^{-1}$]</th>
<th>$\beta_{35}$</th>
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<tr>
<td>CrCl$_6$$^-$</td>
<td>13 200</td>
<td>560</td>
<td>0.61</td>
</tr>
<tr>
<td>CrF$_6$$^-$(b)</td>
<td>13 200</td>
<td>820</td>
<td>0.89</td>
</tr>
<tr>
<td>MnF$_6$$^-$</td>
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<td>0.56</td>
</tr>
<tr>
<td>MoCl$_6$$^-$</td>
<td>19 130</td>
<td>440</td>
<td>0.73</td>
</tr>
<tr>
<td>TcF$_6$$^-$</td>
<td>28 400</td>
<td>530</td>
<td>0.75</td>
</tr>
<tr>
<td>RhBr$_6$$^-$</td>
<td>19 000</td>
<td>280</td>
<td>0.39</td>
</tr>
<tr>
<td>RhCl$_6$$^-$</td>
<td>20 300</td>
<td>350</td>
<td>0.48</td>
</tr>
<tr>
<td>RhF$_6$$^-$$(c)$</td>
<td>22 300</td>
<td>460</td>
<td>0.64</td>
</tr>
<tr>
<td>IrBr$_6$$^-$</td>
<td>23 100</td>
<td>250</td>
<td>0.38</td>
</tr>
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</tr>
<tr>
<td>PtF$_6$$^-$</td>
<td>33 000</td>
<td>380</td>
<td>0.53</td>
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Table 3. Nephelauxetic effect in spin-allowed transitions in hexahalides.

Besides the wellknown nephelauxetic series $F^\rightarrow Cl^\rightarrow Br^\rightarrow I^\rightarrow$, these values also confirm the series of central ions

$\text{Mo(III)} > \text{Cr(III)} > \text{Tc(IV)} > \text{Rh(III)}$

$> \text{Ir(III)} > \text{Mn(IV)} > \text{Pt(IV)}$ (6)

which is somewhat related to the optical electronegativities to be discussed below. However, there is a distinct tendency $d^9 \gg d^8$ and $3d > 5d$ modifying this simple picture of the oxidizing power, i.e. the electron affinity of the partly filled shell of the

central atom, being the only factor of importance for the nephelauxetic effect. There is no doubt that the order Tc(IV) > Mn(IV) for $\beta_{35}$ is more reliable than the inconclusive Tc(IV) ~ Mn(IV) arrived at above for $\beta_{35}$.

Traditionally, the fact that $1 > \beta_{55} > \beta_{35}$ is ascribed to the larger delocalization of the $\sigma$-anti-bonding $\gamma_3$ orbitals than of the $\gamma_5$ sub-shell. Evidence is now accumulating that fluorides have a relatively small difference between $\beta_{55}$ and $\beta_{35}$. Whether this is due to a strong $\pi$-anti-bonding effect of this particular ligand or to a predominance of central-field covalence is not yet clear. Since $\beta_{55}$ and the ratio $\beta_{rel} = (\gamma_{54})_\text{complex}/(\gamma_{54})_\text{gaseous}$ both are 0.83 in ReF$_6^-$ and both are roughly 0.5 in IrF$_6$, it must be concluded the squared Srevess' delocalization coefficient $a^2$ and the Zeff-dependent contribution (proportional to the average value ($r^{-1}$) of the central atom 5d-radial function) must have the same order of magnitude since $20$

$$\beta_{55} \sim a^4 \text{Zeff}^2; \quad \beta_{rel} \sim a^2 (\text{Zeff})^2$$

and hence $a^2 \sim (0.83)^{1/2} = 0.94$ in ReF$_6^-$ and $a^2 \sim (0.5)^{1/2} = 0.79$ in IrF$_6$. On the other hand, ReBr$_6^-$ with $\beta_{55} = 0.64$ and $\beta_{rel} = 0.82$ would suggest $a^2 \sim 0.82$ and hardly any decrease of Zeff. However, it is probable that the partly filled shell of ReBr$_6^-$ is “contaminated” with the large LANDÉ parameter $\zeta_{1p} = 2460$ cm$^{-1}$ of bromine, and hence $\beta_{rel}$ has been exaggerated.

The relativistic splitting of $^4T_2$ and $a^4T_4$ of $\gamma_5^2\gamma_3$ is $\frac{3}{2}\Delta\text{rad}$ to the first order. The expected separation $\sim 600$ cm$^{-1}$ cannot be observed in TcF$_6^-$. According to private communication from Dr. CLAUS SCHÄFFER, University of Copenhagen, it is not even probable that the total width $\sim 1700$ cm$^{-1}$ (cf. ref. 18) predicted for ReF$_6^-$ might be observed, since the half-width $\delta$ of the first, Gaussian-shaped band of TcF$_6^-$ is 1700 cm$^{-1}$, and since superposed Gaussian curves with the same half-width produce a Gaussian-shaped sum curve to a very high approximation.

The second spin-allowed transition, to $a^4T_4$, in ReF$_6^-$ was perhaps covered by traces of ReO$_4^-$ formed by oxidation. We continue the investigation of this particular point.

It is seen from Table 2 that the expected values of $\Delta$ bring the first spin-allowed transition $^4T_2 \to ^4T_3$ in the region of the electron transfer bands of the three heavy halogens. It is doubtful whether shoulders $\sim 26,000$ cm$^{-1}$ of TcCl$_6^-$ and $\sim 28,000$ cm$^{-1}$ of ReCl$_6^-$ represent this transition, or only weak electron transfer bands. Study of crystalline materials at low temperature might perhaps clarify this situation.

**Electron Transfer Bands**

The configuration $^2\pi^3\gamma_5^q+1$ has an energy above the ground configuration $^2\pi^4\gamma_5^q$ which, to a first approximation, is a linearly decreasing function of increasing $q$ and of increasing oxidation number of the central atom. The spin-pairing energy, written as $D[S(S+1)] - S(S+1)$ as a function of the spin quantum number $S$ of the partly filled shell alone contributes a variation which is linear for $q = 3, 4, 5$ but jumps a lower energy of the first electron transfer band of $d^2$ (S changing from 1 to 3/2) to a higher energy of $d^3$ (S(3/2 → 1)). This is the reason why the electron transfer spectra of neutral 5d group hexafluorides change in the order WFe $>$ OsF$_6$ $>$ IrF$_6$ $>$ PtF$_6$. In this approximation, the wavenumbers expected of the first $\pi \to \gamma_3$ and the first $\pi \to \gamma_5$ electron transfer bands are $38$

$$\begin{align*}
d^2: & V - 2(E - A) - \frac{1}{2}D, \quad V + \Delta - 2(E - A) - \frac{1}{2}D, \\
d^3: & V - 3(E - A) + \frac{1}{2}D, \quad V + \Delta - 3(E - A) - 2D, \\
d^4: & V - 4(E - A) + \frac{1}{2}D, \quad V + \Delta - 4(E - A) - \frac{1}{2}D, \\
d^5: & V - 5(E - A) + \frac{3}{2}D, \quad V + \Delta - 5(E - A) - \frac{3}{2}D, \\
d^6: & V + \Delta - 6(E - A) - D
\end{align*}$$

where $V$ is a standard wavenumber for the comparison, $(E - A)$ expresses the gradual stabilization of the $\gamma_5$ orbitals as function of increasing atomic number (keeping the oxidation number constant), and $D$ is inversely proportional to the average radius of the partly filled shell. Actually, $D$ equals $(\frac{2}{3}B + C)$ if only terms with maximum seniority number are considered whereas it is $7/6$ times as large without this restriction. For our purposes, $D$ can be identified with the value of $7B$ in Table 2.

However, we are bound to run into certain difficulties in the detailed assignment of electron transfer spectra. The point is that low-spin $d^5$ complexes are particularly simple, the excited state $^2\pi^3\gamma_5^q$ containing a closed sub-shell with the fractional parentage $^1T_1$. The relativistic effects in the central atom only produce an additional excitation energy $\gamma_3\text{rad}$

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to the electron transfer, because the component $\Gamma_7$ is the groundstate of $2\Gamma_5(\gamma_5^5)$ complexes. The situation is already more complicated in low-spin $d^4$ systems $^9$ which, hypothetically, might arrive as well in $\Gamma_7$ as $\Gamma_8$ components of the excited $\gamma_5^5$ states. However, the latter transitions at higher energy are not perceived because they are essentially two-electron jumps. Hence, the main effect of relativistic effects in the central atom is to add $+\zeta_{\text{nd}}$ to the excitation energy, because the groundstate component $a\Gamma_1$ is a fairly pure $j$, $j$-coupling configuration $\gamma_7^2$ with the relativistic contribution $-2\zeta_{\text{nd}}$, whereas as the excited $\Gamma_7$ component is stabilized half as much, as we saw. The apothecosis of these considerations arrive in octahedral $d^3$-complexes, where the groundstate component $a\Gamma_1$ might be transformed to all seven energy levels ($a\Gamma_1$, $a\Gamma_4$, $a\Gamma_5$, $b\Gamma_4$, $b\Gamma_5$, and $b\Gamma_1$) of $\gamma_5^4$ in the excited configuration $\pi_{\text{23}}\gamma_5^4$. We know from the spectra of OsCl$_6$$^-$, PtF$_6$ and similar complexes $^{11}$ that the total spreading of these seven components is large, some 16 000 cm$^{-1}$. If we consider the very lowest transition possible, $a\Gamma_5 \rightarrow a\Gamma_1$, the first-order contribution from central atom relativistic effects is $-2\zeta_{\text{nd}}$ [hence, we have lost the linear variation with $q$ in eq. (8)] which is partly cancelled by second-order contributions such as $+\zeta_{\text{sq}}(35B)$ from eq. (2). On the other hand, the total spreading of accessible $\pi_{\text{23}}\gamma_5^4$ levels is much larger though it starts $2\zeta_{\text{nd}}$ earlier.

In order to consider the relativistic effects in the ligands, we consider at first the hexachlorides where $\zeta_{\text{sp}}$ is relatively small $^{8,18}$. We remark at once from Figs. 1 and 2 that the spectra of TcCl$_6$$^-$ and ReCl$_6$$^-$ are similar, and rather different from the otherwise so similar $^9$ OsCl$_6$$^-$ and IrCl$_6$$^-$. A further complication comes already from eq. (8) because of the opposite signs to $D$ for $\pi_{\text{23}}\gamma_5^4$ and $\pi_{\text{23}}\gamma_5^3\gamma_3$, the difference $4D$ representing as much as 12 000 cm$^{-1}$ according to Table 2. In other words, the configuration $\pi_{\text{23}}\gamma_5\gamma_3$ is not $\Delta\sim25$ 000 cm$^{-1}$ but only $\sim13$ 000 cm$^{-1}$ (TcCl$_6$$^-$) to $\sim17$ 000 cm$^{-1}$ (ReCl$_6$$^-$) above $\pi_{\text{23}}\gamma_5^4$. Actually, the strongest band of $\pi_{\text{23}}\gamma_5^4\gamma_3$ is situated at 43 100 cm$^{-1}$ in IrCl$_6$$^-$ and at 47 900 cm$^{-1}$ in $^{39}$ OsCl$_6$$^-$ so we extrapolate that this band should occur $\sim53$ 000 cm$^{-1}$ in ReCl$_6$$^-$ outside of the region available here. By the same token, the similar excited level belonging to $\pi_{\text{23}}\gamma_5^4$ should occur at $\sim36$ 000 cm$^{-1}$. This agrees well with the strongest maximum at 35 630 cm$^{-1}$ of ReCl$_6$$^-$.

We are accustomed $^{9,18}$ to find a weak, LAPORTE-forbidden band some 3 000 cm$^{-1}$ before the first LAPORTE-allowed band, and it has been ascribed to the symmetry type even $\gamma_4$ among the twelve $\pi$ orbitals. Hence, at least one of the shoulders of ReCl$_6$$^-$ before 35 650 cm$^{-1}$ should be ascribed to a similar transition; but it is not evident whether all three shoulders have this origin, or whether one is caused by the $\gamma_5^3\rightarrow\gamma_5^4\gamma_3^4\Gamma_5$ transition.

We assume that the strong band of TcCl$_6$$^-$ at 29 580 cm$^{-1}$ has the same origin as the 35 650 cm$^{-1}$ maximum of ReCl$_6$$^-$, and that the precedent shoulder is due to the ($\pi$ even $\gamma_4$) $\rightarrow\gamma_5$ transition. We expect hence the strong ($\pi$ odd $\gamma_4$) $\rightarrow\gamma_5$ transition roughly at 42 000 cm$^{-1}$, and actually, the band at 41 670 cm$^{-1}$ is so intense that it must be ascribed to this transition.

It is quite evident from Figs. 1 and 2 that the more reducing ligands bromide and iodide have the electron transfer spectra at lower wavenumbers, though the shift is slightly smaller than usual. The relativistic effects in the ligands cannot be neglected, and we have the rather confusing combination $^{9,18}$ of twelve $\gamma_j$ components (the first five seem to be even $\gamma_j$, even $\gamma_8$, odd $\gamma_7$, odd $\gamma_9$, and odd $\gamma_5$) of the $\pi$- or $\sigma$-vacancy multiplied by the numerous $\gamma_5^4$ levels. It is already evident $^{46}$ in OsI$_6$$^-$ that hexa­iodides usually have weak electron transfer bands at considerably lower wavenumbers than the LAPORTE-allowed ones. Hence, it is fair to assume that the shoulders at 11 550 and 12 440 cm$^{-1}$ of ReI$_6$$^-$ are due to electron transfer rather than being intensified transitions to $\Gamma_7$ and $d\Gamma_4$ though it is annoying that their wavenumbers are so close to 9 350 and 10 700 cm$^{-1}$ characterizing $^{46}$ OsI$_6$$^-$. However, the intensity distribution is rather unexpected, and it is surprising that TcI$_6$$^-$ does not present similar bands before 10 890 and 11 600 cm$^{-1}$.

The band at 38 300 cm$^{-1}$ of TcBr$_6$$^-$ is so broad that it may consist of several components of the $\pi_{\text{23}}\gamma_5\gamma_3$ excitation which again may explain the intense band at 30 200 cm$^{-1}$ of TcI$_6$$^-$. There is little doubt that this identification also applies to the bands at 28 500 and 34 460 cm$^{-1}$ of ReI$_6$$^-$ (cf. 26 800, 30 000, and 35 600 cm$^{-1}$ for OsI$_6$$^-)$ suggesting that also the band at 22 080 cm$^{-1}$ of TcI$_6$$^-$ has this origin.


It is seen from Figs. 1 and 2 that the electron transfer bands have slightly lower wavenumbers in technetium (IV) than in the corresponding rhenium (IV) hexahalide. If we consider, arbitrarily, the wavenumber where the molar extinction coefficient $\varepsilon$ passes 1 000, it occurs at:

$\text{TcCl}_6^{-} \rightarrow 25 100$; $\text{TcBr}_6^{-} \rightarrow 19 100$; $\text{TcI}_6^{-} \rightarrow 11 700$;
$\text{ReCl}_6^{-} \rightarrow 30 000$; $\text{ReBr}_6^{-} \rightarrow 22 500$; $\text{ReI}_6^{-} \rightarrow 13 200$. (9)

In order to get a quantitative measure of how much more oxidizing is Tc (IV) than Re (IV), we evaluate the optical electronegativity $\alpha_{\text{opt}}$. Table 4 corrects the wavenumber $\sigma$ of the first intense band of the $\tau^2 \gamma^4$ group with 2 $D$ from Table 2 in order to get $\sigma_{\text{corr}}$ which defines for the central atom

$$\sigma_{\text{corr}} = (30 000 \text{ cm}^{-1}) \left[ x_{\text{opt}}(X) - x_{\text{opt}}(M) \right]$$

the values for the ligands being given by $x_{\text{opt}} = 3.00$ for $X = \text{Cl}$, 2.80 for $\text{Br}$, and 2.50 for $I$. It can be concluded that the values of $x_{\text{opt}}(M)$ are

$$2.25 \text{ for } \text{Tc(IV)} \text{ and } 2.05 \text{ for } \text{Re(IV)} \text{ (11)}$$

though $\text{ReI}_6^{-}$ presents a certain irregularity. This may be related to the interesting question 42 whether deviations occur from the normal, linear variation 42 of $x_{\text{opt}}$ as function of $q$ and oxidation number, when $\sigma_{\text{corr}}$ tends towards zero.

Table 4 also corrects $\sigma_{\text{corr}}$ from (eq. 10) further to $\sigma_{\text{corr(rel.)}}$ by the relativistic effect [$2 \xi_{nd} - (\xi_{3d}^2/35 B)$] in the central atom mentioned above. It may be noted that the difference between 4$d^3$ and 5$d^3$ is accentuated by this correction, whereas 4$d^4$ and 5$d^4$ would be brought closer. We remember, however, that $x_{\text{opt}}$ of the ligands referring to the stabler $\tau$ ($\omega = 1/2$) electrons would be about 2.88 in $\text{Br}$ and 2.67 in I, cancelling a part of the differences between the three heavy halogens.

Finally, Table 5 compares $x_{\text{opt}}$ values (without relativistic corrections) in elements close to Tc in the Periodic Table. Unfortunately, such values are not known 42 in the $3d$ group though $x_{\text{opt}}$ of Mn (IV) would be expected to be at least 2.5.

<table>
<thead>
<tr>
<th>$d^3$</th>
<th>$d^4$</th>
<th>$d^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Mo(III)}$</td>
<td>2.25</td>
<td>$\text{Ru(IV)}$</td>
</tr>
<tr>
<td>$\text{Re(IV)}$</td>
<td>2.05</td>
<td>$\text{Os(IV)}$</td>
</tr>
<tr>
<td>$\text{Ir(IV)}$</td>
<td>2.9</td>
<td>$\text{Pt(VI)}$</td>
</tr>
</tbody>
</table>

Table 5. Optical electronegativities $x_{\text{opt}}$ of neighbour elements in the Periodic Table.

**General Conclusions**

Our spectrophotometric studies have confirmed a general impression 12 of technetium (IV) occupying an intermediate position between manganese (IV) and rhenium (IV), but relatively closer to the third element, as one would also expect from the lanthanide contraction of the ionic radii. The utility of M.O. treatment of inorganic chromophores 43, 44 has been demonstrated once more. The one- and two-electron parameters have allowed the following conclusions:

1. The optical electronegativity $x_{\text{opt}}$ derived from the electron transfer bands is 2.25 for $\text{Tc(IV)}$ and 2.05 for $\text{Re(IV)}$. Hence, the more oxidizing $\text{Tc(IV)}$ is expected to have a slightly greater tendency towards covalent bonding, and actually,

2. The nephelauxetic effect is slightly greater for the intra-sub-shell transitions of $\text{Tc(IV)}$ than $\text{Re(IV)}$. However, the influence of the ligands is far larger; the hexaiodides have a much smaller nephelauxetic ratio $\beta_{55}$ than the hexafluorides. It may be mentioned that the influence of oxidation number is even more conspicuous than that of the ligands; $\text{IrF}_6$ has a smaller $\beta_{55}$ than $\text{TcI}_6^{-}$.

3. Though partly covalent bonding subsists, the complexes studied can be shown not to obey the principle of electroneutrality 20. A lower limit for the residual positive charge [assuming $a^2$ of eq. (7)] equal to one, i.e. no delocalization of the partly fil-

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42 C. K. Jørgensen, Mol. Phys. 6, 43 [1963].
led shell due to symmetry-restricted covalency] would be 2.5 for TcF₆⁻, 1.5 for TcCl₆⁻, 1.0 for TcI₆⁻, 2.8 for ReF₆⁻, 1.7 for ReCl₆⁻, and 1.2 for IrF₆⁻. Actually, there are good reasons to believe that the central field rather affects the partly filled d shell as if the central ion carried a charge somewhere between these minimum values and the integers representing the oxidation numbers.

4. The spectrochemical parameter \( \Delta \) has been determined in TcF₆⁻ and ReF₆⁻, showing the usual increase with principal quantum number (the two values are 1.31 and 1.51 times as large, respectively, as for MnF₆⁻⁻).

5. The blurring out of the vibrational structure suggests minor deviations from regular octahedral symmetry. These deviations were previously known in K₂ReCl₆ subject to high pressure, (cf. also ref. 31) and seem to be more important in Tc(IV) hexahalides in aqueous solution, perhaps because of the smaller ionic radius.

It would be interesting to extend the spectroscopic studies to isoelectronic species such as RuF₆⁻, the tetrameric ⁴⁵ Ru₄F₂₀, and RhF₆ gas. These species are expected ⁴⁵ to show a pronounced nephelauxetic effect, and the optical electronegativities \( x_{\text{opt}} = 2.7 \) for Ru(V) and 3.1 for Rh(VI). It is remarkable that it has been possible to investigate TcI₆⁻⁻; this species might have been expected to be reduced by I⁻, or be hydrolyzed more rapidly. Chemically, Tc(IV) joins the platinum metals to some extent, like Re(IV), though technetium certainly has the great tendency to form mononuclear or polymeric ozono-complexes ¹⁴ also characterizing Mo(V), Ru(VI), Os(VI), and before all, Re(IV) and Re(V). On the other hand, Tc(IV) hexahalides are, except for their radioactivity, far easier to handle than species such as MoCl₆⁻⁻ and MoCl₆⁻ which only have been studied recently ⁴⁶, ⁴⁷. Actually, the absorption spectra of nearly all hexahalides known to exist in solution have been studied now; in addition to the discussion ⁹ of Ru(III), Ru(IV), Rh(III), Rh(IV) ⁴¹, Pd(IV), Sn(IV), Sb(V), W(VI), Re(IV), Os(III) ⁴⁰, Os(IV), Ir(III), Ir(IV) ¹⁸, Pt(IV), and Pb(IV) came recently the interpretation ⁴⁸ of U(IV), Np(IV), and Pu(IV) hexahalides.

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