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

CHR. KLIXBÜLL JØRGENSEN

Cyanamid European Research Institute, Cologny (Geneva), Switzerland

and KLAUS SCHWOCHAU

Arbeitsgruppe „Institut für Radiochemie“ der Kernforschungsanlage Jülich,
at present situated in Institut für Kernchemie der Universität Köln, Germany

(Z. Naturforschg. **20 a**, 65—75 [1965]; eingegangen am 17. Juli 1964)

Absorption spectra of aqueous solutions of TcX_6^{--} and ReX_6^{--} (X=F, Cl, Br, I) are measured between 8 000 and ~ 50 000 cm^{-1} and theoretically discussed. The electron transfer spectra indicate the optical electronegativity $x_{opt}=2.25$ for Tc(IV) and 2.05 for the less oxidizing Re(IV). The spectrochemical parameter Δ is determined to 28 400 cm^{-1} in TcF_6^{--} and 32 800 cm^{-1} in ReF_6^{--}. The nephelauxetic effect is evaluated from the spin-forbidden intra-sub-shell transitions in all eight species, and from the two spin-allowed bands of TcF_6^{--}. The vibrational structure of the narrow absorption bands and the possible weak distortion from octahedral symmetry of Tc(IV) hexahalides are discussed.

Technetium(IV) hexahalides have a considerable theoretical interest, because they represent d^3-systems known to have very detailed absorption spectra with more experimental features than parameters for the description of the transitions in the partly filled shell[1, 2]. The isoelectronic molybdenum(III) is known[1, 3] in $MoCl_6^{-3}$ and a few other compounds, whereas technetium(IV) only has been subject of a few publications[4, 5]. The articles on absorption spectra of rhenium(IV) are more numerous[6–11]. Recently, one of the writers published a review[12] on Tc containing a figure with preliminary data on spectra of TcX_6^{--} which provoked the other writer to attempt a theoretical treatment.

Experimental

The potassium technetium(IV) hexahalides were prepared from $K^{99}TcO_4$ by previously described methods[12, 13] and recrystallized. The analogous rhenium(IV) compounds were prepared according to methods well known in the literature.

The tendency towards hydrolysis becomes much stronger in the direction from the chloro to the iodo complexes and is more pronounced for Tc(IV) than for Re(IV). Hence, it is necessary to use rather concentrated hydrogen halide solutions.

The fluoride complexes were measured in water (actually, ReF_6^{--} has some tendency to form ReO_4^- by oxidation, disturbing the spectrum above 40 000 cm^{-1}), the chlorides in 10% aqueous HCl, the bromides in 24% HBr and the iodides in 57% iodine-free HI. It is necessary to measure quickly the spectra of the rapidly hydrolyzing iodide solutions.

The absorption spectra in the near infra-red and the visible were measured on a Cary 14 spectrophotometer, whereas a Zeiss-RPQ 20-spectrometer was used for recording the ultraviolet spectra.

Discussion

On Figs. 1 and 2, and in Table 1, one recognizes clearly three types of absorption bands:

(1) The narrow, very weak absorption bands, some with vibrational structure, which are caused by transitions within the lowest sub-shell γ_5^3 between the groundstate $^4\Gamma_2$ (in BETHE's notation; $^4A_{2g}$ in MULLIKEN's notation) to the excited levels

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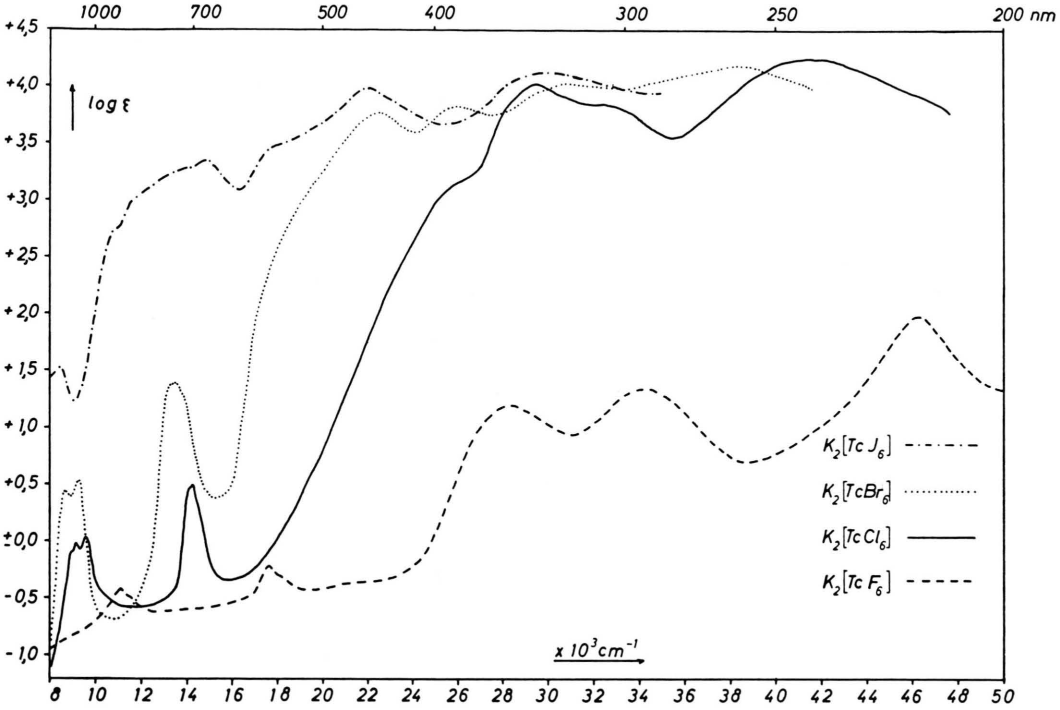

Fig. 1. Absorption spectra of technetium (IV) hexahalides.

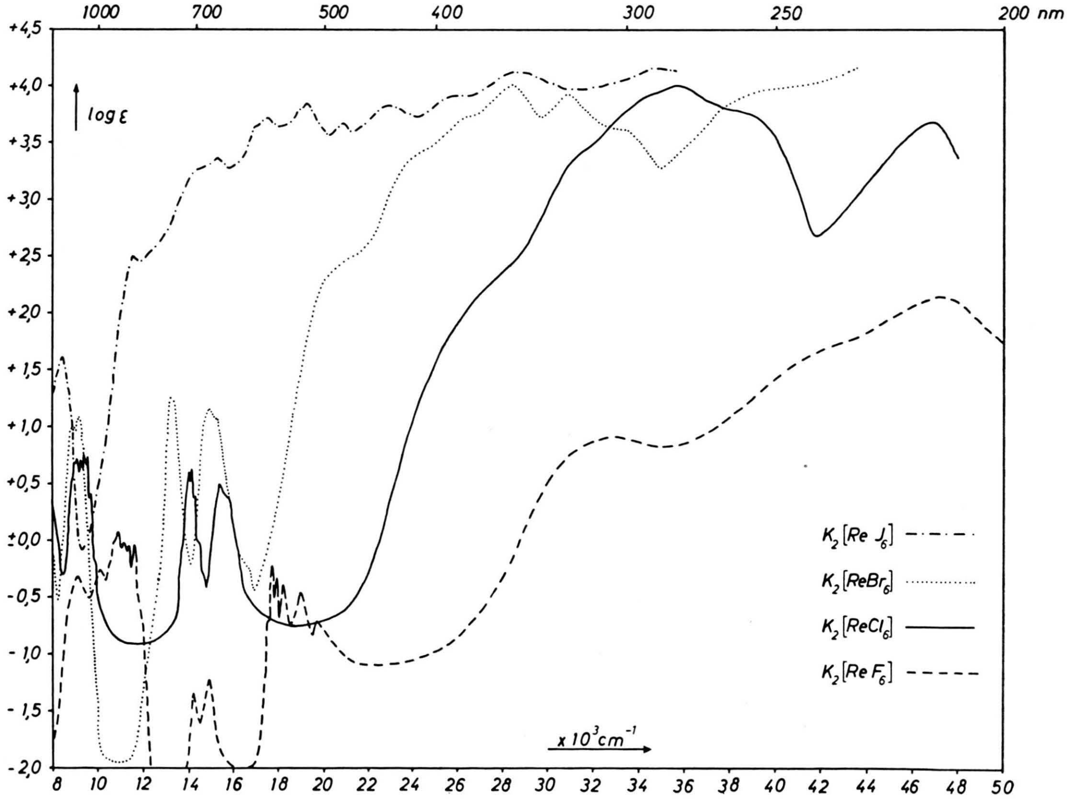

Fig. 2. Absorption spectra of rhenium (IV) hexahalides.

Wave-length λ in mμ	Wavenumber σ in units of 1000 cm^{-1}	Extinction coefficient ε_λ [mol^{-1} l cm^{-1}]	Assignment
$\mathrm{TcF_6^{--}}$			
907	11.03	0.38	$^2\Gamma_3$ and $^3\Gamma_4$
(871)	(11.48)	0.32	
568	17.61	0.60	$^2\Gamma_5$
(553)	(18.08)	0.49	
~ 470	21.3	0.5	(?)
352	28.41	15.8	$^4\Gamma_5$
291	34.36	21.9	$a\,^4\Gamma_4$
216	46.3	100	(?)
$\mathrm{TcCl_6^{--}}$			
(1121)	(8.92)	0.78	vibrational structure $^2\Gamma_3$ and $^2\Gamma_4$
1095	9.13	0.95	
1046	9.56	1.09	
(1031)	(9.70)	0.99	
709	14.10	2.91	$^2\Gamma_5$
704	14.20	3.01	
(385)	(25.97)	1380	$\pi\,(\text{even }\gamma_4) \to \gamma_5$
338	29.58	10600	$\pi\,(\text{odd }\gamma_4) \to \gamma_5$
(308)	(32.47)	7130	$\pi \to \gamma_5$
240	41.67	18000	$\pi\,(\text{odd }\gamma_4) \to \gamma_3$
$\mathrm{TcBr_6^{--}}$			
1153	8.67	2.74	$^2\Gamma_3$ and $^2\Gamma_4$
1082	9.24	3.41	
754	13.26	23.5	$^2\Gamma_5$
744	13.44	24.1	
726	13.77	19.4	
443	22.55	5750	$\pi \to \gamma_5$
385	26.00	6650	$\pi \to \gamma_5$
325	30.79	10160	
287	34.84	11220	
261	38.29	15450	$\pi\,(\text{odd }\gamma_4) \to \gamma_3$
$\mathrm{TcI_6^{--}}$			$^2\Gamma_3$ and $^2\Gamma_4$
1178	8.49	33	
(918)	(10.89)	540	
(862)	(11.60)	850	
713	14.03	1850	$\pi \to \gamma_5$
671	14.90	2170	$\pi \to \gamma_5$
(557)	(17.96)	2970	$\pi \to \gamma_5$
453	22.08	9660	$\pi \to \gamma_3$?
331	30.20	13540	$\pi \to \gamma_3$
$\mathrm{ReF_6^{--}}$			
1101	9.08	0.47	$b\,\Gamma_8$
987	10.13	0.56	vibrational structure $c\Gamma_8$ and Γ_6
952	10.50	0.61	
(935)	(10.69)	0.92	
918	10.89	1.19	
896	11.16	0.94	
878	11.39	0.89	
864	11.57	0.90	
(843)	(11.86)	0.23	
704	14.20	0.04	co-excited vibrations
672	14.88	0.06	
(572)	(17.48)	0.19	vibrational structure Γ_7
566	17.67	0.59	
559	17.89	0.45	
549	18.22	0.40	
529	18.91	0.36	$d\Gamma_8$
507	19.72	0.19	
305	32.80	7.65	$^4\Gamma_5$
(267)	(37.5)	10.4	$a\,^4\Gamma_4$
(240)	(41.7)	38	?
207	48.3	182	?
$\mathrm{ReCl_6^{--}}$			
1315	7.60	3.01	$b\,\Gamma_8$
(1134)	(8.82)	3.08	vibrational structure $c\,\Gamma_8$ and Γ_6
1113	8.99	4.75	
1100	9.09	5.21	
1078	9.28	5.00	
1062	9.42	5.55	
1046	9.56	5.49	
1030	9.71	2.56	
1014	9.86	0.70	
(729)	(13.72)	0.79	
(719)	(13.91)	2.58	vibrational structure
714	14.01	3.97	
707	14.14	4.21	Γ_7
700	14.29	2.44	
(691)	(14.47)	0.90	
(682)	(14.66)	0.48	
652	15.34	3.08	$d\,\Gamma_8$
(632)	(15.82)	2.30	
(357)	(28.01)	227	$^4\Gamma_5$?
(316)	(31.65)	2880	$\pi \to \gamma_5$
(293)	(34.08)	7410	$\pi \to \gamma_5$
281	35.65	11980	$\pi\,(\text{odd }\gamma_4) \to \gamma_5$
(256)	(39.12)	5580	
213	46.88	4960	
$\mathrm{ReBr_6^{--}}$			
1377	7.26	6.81	$b\,\Gamma_8$
1319	7.58	5.93	
1132	8.83	9.52	vibrational structure $c\,\Gamma_8$ and Γ_6
1116	8.96	9.52	
1097	9.12	11.36	
1091	9.17	12.00	
1084	9.23	11.00	
1069	9.36	6.78	
756	13.23	18.1	Γ_7
750	13.33	17.3	
673	14.86	14.8	$d\,\Gamma_8$
658	15.20	11.7	
598	16.72	0.5	co-excited vibration
(478)	(20.92)	214	$\pi\,(\text{odd }\gamma_4) \to \gamma_5$
(417)	(23.98)	2450	$\pi \to \gamma_5$
(379)	(26.39)	5370	$\pi \to \gamma_5$
352	28.38	10170	$\pi \to \gamma_5$
324	30.88	8810	
(302)	(33.06)	4340	
253	39.60	9260	
$\mathrm{ReI_6^{--}}$			
~ 1350	~ 7.35	8	$b\,\Gamma_8$
1181	8.47	40	$c\,\Gamma_8$ and Γ_6
866	11.55	320	$\pi \to \gamma_5$
(804)	(12.44)	360	
(690)	(14.50)	1860	$\pi \to \gamma_5$
659	15.18	2280	
(592)	(16.88)	4310	
572	17.49	5090	
(533)	(18.77)	6140	
520	19.23	6850	
481	20.78	4700	
(457)	(21.88)	5850	
444	22.52	6920	
434	23.04	6980	
(423)	(23.64)	6280	
387	25.87	8190	$\pi \to \gamma_3$?
350	28.50	13100	$\pi \to \gamma_3$
290	34.46	14700	$\pi \to \gamma_3$

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.

$^2\Gamma_3$ and $^2\Gamma_4$ (which are nearly coincident[15] if the γ_5 orbitals have angular functions characterizing $l=2$) and $^2\Gamma_5$. If the relativistic effects are predominant, i. e. the LANDÉ parameter ζ_{nd} of the central atom is large, as is the case for Re, a weak splitting into five excited components is predicted[10, 16].

(2) Broad but relatively weak bands, caused by the spin-allowed transitions to the two levels $^4\Gamma_5$ and $a\,^4\Gamma_4$ belonging to the excited sub-shell configuration $\gamma_5{}^2\,\gamma_3$. Because a weakly π-anti-bonding γ_5 electron is transferred to the highly σ-anti-bonding γ_3 orbital, the internuclear distances at equilibrium of the excited electronic state are increased[17] 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[1]. 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 σ and twelve π) on the ligands to the partly filled shell. The lowest excited configuration type is $\sigma^{12}\,\pi^{23}\,\gamma_5{}^4$ whereas configurations such as $\sigma^{12}\,\pi^{23}\,\gamma_5{}^3\,\gamma_3$ or $\sigma^{11}\,\pi^{24}\,\gamma_5{}^3\,\gamma_3$ have higher energy[9]. It is possible to apply molecular orbital (M.O.) theory to these electron transfer spectra[2, 9] 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 ζ_{np}. Since the internuclear distances at the minimum of the potential surfaces belonging to the configurations $\sigma^{12}\,\pi^{24}\,\gamma_5{}^3$ and $\sigma^{12}\,\pi^{23}\,\gamma_5{}^4$ do not seem very different, the first electron transfer bands can be relatively narrow[18].

Intra-sub-shell Transitions

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

$$\begin{array}{c} ReI_6^{--} < ReBr_6^{--} < ReCl_6^{--} < ReF_6^{--} \\ TcI_6^{--} < TcBr_6^{--} < TcCl_6^{--} < TcF_6^{--} \end{array} \qquad (1)$$

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 π-orbitals; iodide is more reducing than fluoride[19]. 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*[20], i. e. the cloud-expanding of the d-shell participating in the formation of σ-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[21]. 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 $^4\Gamma_2$ than in the excited levels.

To the first approximation[15, 22, 23] the energy difference from $^4\Gamma_2$ to $^2\Gamma_3$ and $^2\Gamma_4$ is $3\,K\,(4,5)$ and from $^4\Gamma_2$ to $^2\Gamma_5$ is $5\,K\,(4,5)$ where the "exchange integral" $K\,(4,5)$ represents $(3\,B+C)$ 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

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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 $\gamma_5\gamma_3{}^2$ than $^2\Gamma_3$ and $^2\Gamma_4$. This discrepancy was first discussed by TANABE and SUGANO [15]. In the Re(IV) and Ir(VI) hexahalides, the relativistic effects are more important, corresponding to a larger value of the LANDÉ parameter $\zeta_{5\mathrm{d}}$ of the central atom, and we denote the separated components with BETHE's double-group quantum numbers, the groundstate $^4\Gamma_2$ being $a\,\Gamma_8$, the nearly coincident $^2\Gamma_3$ and $^2\Gamma_4$ becoming $b\,\Gamma_8$, $c\,\Gamma_8$ and Γ_6, and $^2\Gamma_5$ separating in Γ_7 and $d\,\Gamma_8$. If second-order perturbation theory is applied to EISENSTEIN's determinants [10] the approximate energy turns out to be, assuming $C = 4\,B$,

$$\begin{aligned}
a\,\Gamma_8&: \quad -\frac{\zeta^2}{35\,B}-\frac{3\,\zeta^2}{\Delta},\\
b\,\Gamma_8&: \quad 21\,B-\frac{5\,\zeta^2}{56\,B}-k_1\frac{B^2}{\Delta}-\frac{3\,\zeta^2}{\Delta},\\
c\,\Gamma_8&: \quad 21\,B-k_2\frac{B^2}{\Delta}-\frac{3\,\zeta^2}{\Delta},\\
\Gamma_6&: \quad 21\,B-24\frac{B^2}{\Delta}-\frac{3\,\zeta^2}{\Delta},\\
\Gamma_7&: \quad 35\,B-176\frac{B^2}{\Delta}-\frac{3\,\zeta^2}{\Delta},\\
d\,\Gamma_8&: \quad 35\,B+\frac{33\,\zeta^2}{280\,B}-176\frac{B^2}{\Delta}-\frac{3\,\zeta^2}{\Delta}.
\end{aligned}\tag{2}$$

Second-order perturbation theory [1] 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 $^2\Gamma_3$ and $^2\Gamma_4$ is negligible compared to ζ^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 $\gamma_5{}^3$, viz. $-3\,\zeta^2/\Delta$, 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 ζ 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 $^2\Gamma_3$ comes from a particularly large non-diagonal element of interelectronic repulsion, i. e. $\sqrt{72}\,B$ with one of the two $^2\Gamma_3$ levels of $\gamma_5{}^2\gamma_3$, which happens to be as high as $\Delta+26\,B$ and not only Δ above the energy of the unperturbed $^2\Gamma_3$ of $\gamma_5{}^3$. Hence, the usual second-order perturbation expression for the energy of $^2\Gamma_3$, $21\,B-90\,B^2/\Delta$, tends to exaggerate the depression, especially in chromium(III) complexes with low values of Δ/B, by a factor roughly two.

We have a rather indirect way to determine $\zeta_{5\mathrm{d}}$ in our rhenium(IV) complexes and in IrF_6 studied by MOFFITT, GOODMAN, FRED and WEINSTOCK [24, 25]: to put the observed energy difference between the Γ_7 and $d\,\Gamma_8$ components equal to $33\,\zeta^2/280\,B$ according to eq. (2). The values obtained,

$$\begin{aligned}
&3\,100\ \mathrm{cm}^{-1}\ \mathrm{IrF}_6; &&2\,450\ \mathrm{cm}^{-1}\ \mathrm{ReBr}_6{}^{--};\\
&2\,400\ \mathrm{cm}^{-1}\ \mathrm{ReCl}_6{}^{--};\ \text{and} &&2\,550\ \mathrm{cm}^{-1}\ \mathrm{ReF}_6{}^{--}
\end{aligned}\tag{3}$$

are rather uncertain, ±20%. They may be compared to the values $\zeta_{5\mathrm{d}}=3\,500\ \mathrm{cm}^{-1}$ for gaseous [22] ReF_6, $3\,400\ \mathrm{cm}^{-1}$ for gaseous [24] OsF_6, and $2\,800\ \mathrm{cm}^{-1}$ for [11] $OsCl_6{}^{--}$. JOHANNESEN and CANDELA [26] 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 $\zeta_{5\mathrm{d}}=2\,100\ \mathrm{cm}^{-1}$ for $OsCl_6{}^{--}$ and $OsBr_6{}^{--}$.

It is known from gaseous ions [27] and from the relative intensities of spin-forbidden and spin-allowed transitions in Mo(III) complexes that the order of magnitude expected for $\zeta_{4\mathrm{d}}$ in Tc(IV) complexes is 1 000 cm^{-1}. Hence, the energy difference $33\,\zeta^2/280\,B$ between the components Γ_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 β_{55} between the value for $7\,B$ derived for the complexes according to eq. (2) and the values known or extrapolated for the gaseous ions [1], viz. $7\,B = 7\,450\ \mathrm{cm}^{-1}$ for Mn^{+4}, 4 260 cm^{-1} for Mo^{+3}, 4 930 cm^{-1} for Tc^{+4}, 4 550 cm^{-1} for Re^{+4}, and 5 670 cm^{-1} for Ir^{+6}. In all cases, a moderate nephelauxetic ratio β_{55} 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 β_{55} 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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	Δ	$7B$ derived from $^4\Gamma_2 \rightarrow {}^2\Gamma_3, {}^2\Gamma_4$ or $a\Gamma_8 \rightarrow c\Gamma_8$	$7B$ derived from $^4\Gamma_2 \rightarrow {}^2\Gamma_5$ or $a\Gamma_8 \rightarrow \Gamma_7$	Average value $7B$	Nephelauxetic ratio β_{55}
MnF_6^{--}	21750	5950	—	5950	0.82
$MoCl_6^{---}$	19150	3460	3260	3350	0.79
TcF_6^{--}	28400	3930	3870	3900	0.79
$TcCl_6^{--}$	~ 25000	3320	3110	3200	0.65
$TcBr_6^{--}$	~ 24000	3180	2940	3050	0.62
TcI_6^{--}	~ 22000	2970	—	2900	0.59
ReF_6^{--}	32800	3760	3850	3800	0.83
$ReCl_6^{--}$	~ 29000	3100	3040	3100	0.68
$ReBr_6^{--}$	~ 28000	2990	2860	2900	0.64
ReI_6^{--}	~ 26000	2900	—	2850	0.62
IrF_6	~ 36000	2670	2650	2650	0.47

Table 2. Nephelauxetic effect in spin-forbidden intra-sub-shell transitions in octahedral d^3-complexes. Energies in cm^{-1}.

concluded that MnF_6^{--} is less nephelauxetic than TcF_6^{--}; SCHNEIDER's phenomenon mentioned above tends to decrease β_{55} of Mn(IV) by a few percent. The values of Δ are in certain cases (~ signs) extrapolated from well-known properties of the spectrochemical series[1]. Actually, the correction factors $(1-3B/\Delta)$ and $(1-5B/\Delta)$ which can be derived from eq. (2) [$5B/\Delta$ representing $176B^2/(35B\Delta)$, 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 $ReCl_6^{--}$ 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 Γ_7 is equidistant with $\sigma_c = 150\ cm^{-1}$. The same is true[11] for the transition $a\Gamma_1(^3\Gamma_4) \rightarrow b\Gamma_1(^1\Gamma_1)$ of $OsCl_6^{--}$ at $17\,250\ cm^{-1}$ 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 MCl_6^{--} is rather exactly half one of the stretching frequencies. Thus, the bending even Γ_5 mode has the vibrational quantum $158\ cm^{-1}$ in $SnCl_6^{--}$ and $162\ cm^{-1}$ in $PtCl_6^{--}$ whereas the totally symmetric stretching even Γ_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]:

$$
\begin{array}{ll}
ReCl_6^{--} & 346,\ 275,\ 313,\ 172,\ 159; \\
ReBr_6^{--} & 213,\ 174,\ 217,\ 118,\ 104.
\end{array}
\tag{4}
$$

Hence, the more normal situation seems to be the rather profuse superposition of several of the three odd and three even normal modes observed[24] in IrF_6. Our new results further support this opinion. Thus, the distances between individual vibrational levels vary between $180\ cm^{-1}$ and $370\ cm^{-1}$ in the $(c\Gamma_8 + \Gamma_6)$ group of ReF_6^{--}, and the three distances observed in the Γ_7 group of ReF_6^{--} are 190, 210, and $330\ cm^{-1}$. The situation is even more extreme in TcF_6^{--} where splittings into two broad components, $450\ cm^{-1}$ in the near infra-red and $470\ cm^{-1}$ in the yellow-green, are observed. The three distances in the near infra-red of $TcCl_6^{--}$ are 210, 430, and $140\ cm^{-1}$, again far removed from forming an equidistant progression.

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

$$
\begin{array}{ll}
K_2TcF_6:\ 574\ cm^{-1}; & Rb_2TcCl_6:\ 333\ cm^{-1}; \\
K_2ReF_6:\ 550\ cm^{-1}; & Rb_2ReCl_6:\ 319\ cm^{-1};
\end{array}
\tag{5}
$$

presumably caused by the odd Γ_4 stretching mode. They may be compared with the lines[30] at $294\ cm^{-1}$ in salts of $SnCl_6^{--}$, 300 and $314\ cm^{-1}$ for $ReCl_6^{--}$, 304 and $318\ cm^{-1}$ for $OsCl_6^{--}$, 316 and $324\ cm^{-1}$ for $IrCl_6^{--}$, and $330\ cm^{-1}$ for $PtCl_6^{--}$, whereas the 4d group hexahalides are represented[30] by $293\ cm^{-1}$ for $ZrCl_6^{--}$, $332\ cm^{-1}$ for $RuCl_6^{--}$, and $336\ cm^{-1}$ for $PdCl_6^{--}$. 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 M – F stretching

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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.[30], 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[31] 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 γ_5^3 is especially stable towards splitting of the energy levels occurring in cubic symmetry[32]. 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[33]. STEPHENS and DRICKAMER[34] found that the two components of $d\Gamma_8$ of K_2ReCl_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[11] 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 ~3 760 cm^{-1}. The broad and extremely weak band ~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 ${}^4\Gamma_5$ and $a\,{}^4\Gamma_4$ observed in the reflection spectrum[35] of K_2MnF_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 Δ, the one-electron energy difference between the two sub-shell γ_5 and γ_3, and the distance between the two bands[36] 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 β_{35} is 0.75, slightly smaller than the value $\beta_{55} = 0.79$. Table 3 compiles values of B and β_{35} derived from spin-allowed transitions in TcF_6^{--} and a series of related complexes.

	Δ[cm^{-1}]	B[cm^{-1}]	β_{35}
$CrCl_6^{---}$(a)	13200	560	0.61
CrF_6^{---}(b)	15200	820	0.89
MnF_6^{--}	21750	600	0.56
$MoCl_6^{---}$	19150	440	0.73
TcF_6^{--}	28400	530	0.75
$RhBr_6^{---}$	19000	280	0.39
$RhCl_6^{---}$	20300	350	0.48
RhF_6^{---}(c)	22300	460	0.64
$IrBr_6^{---}$	23100	250	0.38
$IrCl_6^{---}$	25000	300	0.46
PtF_6^{--}	33000	380	0.53

(a) W. E. HATFIELD, R. C. FAY, C. E. PFLUGER, and T. S. PIPER, J. Amer. Chem. Soc. **85**, 265 [1963].
(b) C. E. SCHÄFFER and C. K. JØRGENSEN, J. Inorg. Nucl. Chem. **8**, 143 [1958].
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Table 3. Nephelauxetic effect in spin-allowed transitions in hexahalides.

Besides the wellknown nephelauxetic series $F^- \gg Cl^- > Br^-$, these values also confirm the series of central ions

$$\mathrm{Mo(III)} > \mathrm{Cr(III)} > \mathrm{Tc(IV)} > \mathrm{Rh(III)} > \mathrm{Ir(III)} > \mathrm{Mn(IV)} > \mathrm{Pt(IV)} \qquad (6)$$

which is somewhat related to the optical electronegativities to be discussed below. However, there is a distinct tendency $d^3 \gg d^6$ and 3d > 5d modifying this simple picture of the oxidizing power, i. e. the electron affinity of the partly filled shell of the

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central atom, being the only factor of importance for the nephelauxetic effect. There is no doubt that the order Tc(IV) $\gg$ Mn(IV) for β_{35} is more reliable than the inconclusive Tc(IV) $\sim$ Mn(IV) arrived at above for β_{55}.

Traditionally [20, 22] the fact that $1 > \beta_{55} > \beta_{35}$ is ascribed to the larger delocalization of the σ-anti-bonding γ_3 orbitals than of the γ_5 sub-shell. Evidence is now accumulating that fluorides have a relatively small difference between β_{55} and β_{35}. Whether this is due to a strong π-anti-bonding effect of this particular ligand [37] or to a predominance of central-field covalence is not yet clear. Since β_{55} and the ratio $\beta_{\mathrm{rel}} = (\zeta_{5\mathrm{d}})\mathrm{complex}/(\zeta_{5\mathrm{d}})$ gaseous ion both are 0.83 in $\mathrm{ReF_6^{--}}$ and both are roughly 0.5 in $\mathrm{IrF_6}$, it must be concluded the squared STEVENS' delocalization coefficient a^2 and the Z_{eff}-dependent contribution (proportional to the average value $\langle r^{-1} \rangle$ of the central atom 5d-radial function) must have the same order of magnitude since [20].

$$\beta_{55} \sim a^4 Z_{\mathrm{eff}}; \qquad \beta_{\mathrm{rel}} \sim a^2 (Z_{\mathrm{eff}})^2 \tag{7}$$

and hence $a^2 \sim (0.83)^{1/3} = 0.94$ in $\mathrm{ReF_6^{--}}$ and $a^2 \sim (0.5)^{1/3} = 0.79$ in $\mathrm{IrF_6}$. On the other hand, $\mathrm{ReBr_6^{--}}$ with $\beta_{55} = 0.64$ and $\beta_{\mathrm{rel}} = 0.82$ would suggest $a^2 \sim 0.82$ and hardly any decrease of Z_{eff}. However, it is probable [2] that the partly filled shell of $\mathrm{ReBr_6^{--}}$ is "contaminated" with the large LANDÉ parameter $\zeta_{4\mathrm{p}} = 2\,460$ cm^{-1} of bromine, and that hence β_{rel} has been exaggerated.

The relativistic splitting of $^4\Gamma_5$ and $a\,^4\Gamma_4$ of $\gamma_5{}^2\gamma_3$ is $\frac{2}{3}\,\zeta_{n\mathrm{d}}$ to the first order. The expected separation ~ 600 cm^{-1} cannot be observed in $\mathrm{TcF_6^{--}}$. According to private communication from Dr. CLAUS SCHÄFFER, University of Copenhagen, it is not even probable that the total width $\sim 1\,700$ cm^{-1} (cf. ref. [16]) predicted for $\mathrm{ReF_6^{--}}$ might be observed, since the half-width $\delta(-)$ of the first, GAUSSIAN-shaped band of $\mathrm{TcF_6^{--}}$ is 1 700 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 $a\,^4\Gamma_4$, in $\mathrm{ReF_6^{--}}$ was perhaps covered by traces of $\mathrm{ReO_4^-}$ formed by oxidation. We continue the investigation of this particular point.

It is seen from Table 2 that the expected values of Δ bring the first spin-allowed transition $^4\Gamma_2 \rightarrow {}^4\Gamma_5$ in the region of the electron transfer bands of the three heavy halogens. It is doubtful whether shoulders $\sim 26\,000$ cm^{-1} of $\mathrm{TcCl_6^{--}}$ and $\sim 28\,000$ cm^{-1} of $\mathrm{ReCl_6^{--}}$ 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 $\pi^{23}\gamma_5{}^{q+1}$ has an energy above the ground configuration $\pi^{24}\gamma_5{}^q$ which, to a first approximation [9], is a linearly decreasing function of increasing q and of increasing oxidation number of the central atom. The spin-pairing energy [2, 37] written as $D[\langle S(S+1)\rangle - S(S+1)]$ 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 $3/2 \rightarrow 1$). This is the reason why the electron transfer spectra of neutral 5d group hexafluorides [24] change in the order $\mathrm{WF_6} > \mathrm{OsF_6} \sim \mathrm{IrF_6} > \mathrm{PtF_6}$. In this approximation, the wavenumbers expected of the first $\pi \rightarrow \gamma_5$ and the first $\pi \rightarrow \gamma_3$ electron transfer bands are [38]:

$$\begin{array}{lll}
\mathrm{d}^2: & V - 2(E-A) - \frac{4}{3}D, & V + \Delta - 2(E-A) - \frac{4}{3}D, \\
\mathrm{d}^3: & V - 3(E-A) + 2\,D, & V + \Delta - 3(E-A) - 2\,D, \\
\mathrm{d}^4: & V - 4(E-A) + \frac{4}{3}D, & V + \Delta - 4(E-A) - \frac{5}{3}D, \\
\mathrm{d}^5: & V - 5(E-A) + \frac{2}{3}D, & V + \Delta - 5(E-A) - \frac{4}{3}D, \\
\mathrm{d}^6: & - & V + \Delta - 6(E-A) - D
\end{array} \tag{8}$$

where V is a standard wavenumber for the comparison, $(E-A)$ expresses the gradual stabilization of the γ_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 $(\frac{5}{2}B + C)$ if only terms with maximum seniority number are considered [2] whereas it is 7/6 times as large without this restriction. For our purposes, D can be identified with the value of $7\,B$ 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 $\pi^{23}\gamma_5{}^6$ containing a closed sub-shell with the fractional parentage $^1\Gamma_1$. The relativistic effects in the central atom only produce an additional excitation energy $+\zeta_{n\mathrm{d}}$

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[38] C. K. JØRGENSEN, Acta Chem. Scand. **16**, 2406 [1962].

to the electron transfer, because the component Γ_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 Γ_7 as Γ_8 components of the excited γ_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 $+\zeta_{nd}$ to the excitation energy, because the groundstate components $a\,\Gamma_1$ is a fairly pure *j, j*-coupling configuration γ_7^2 with the relativistic contribution $-2\,\zeta_{nd}$, whereas the excited Γ_7 component is stabilized half as much, as we saw. The apotheosis of these considerations arrive in octahedral d^3-complexes, where the groundstate $a\,\Gamma_8(^4\Gamma_2)$ might be transformed to all seven energy levels ($a\,\Gamma_1$, Γ_4, $a\,\Gamma_3$, $a\,\Gamma_5$, $b\,\Gamma_3$, $b\,\Gamma_5$ and $b\,\Gamma_1$) of γ_5^4 in the excited configuration $\pi^{23}\gamma_5^4$. 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, $a\,\Gamma_8 \rightarrow a\,\Gamma_1$, the first-order contribution from central atom relativistic effects is $-2\,\zeta_{nd}$ [hence, we have lost the linear variation with q in eq. (8)] which is partly cancelled by second-order contributions such as $+\zeta^2/(35\,B)$ from eq. (2). On the other hand, the total spreading of accessible $\pi^{23}\gamma_5^4$ levels is much larger though it starts $2\,\zeta_{nd}$ earlier.

In order to separate the relativistic effects in the ligands, we consider at first the hexachlorides where ζ_{3p} is relatively small [9, 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 $\pi^{23}\gamma_5^4$ and $\pi^{23}\gamma_5^3\gamma_3$, the difference $4\,D$ representing as much as 12 000 cm^{-1} according to Table 2. In other words, the configuration $\pi^{23}\gamma_5^3\gamma_3$ is not $\Delta \sim 25\,000$ cm^{-1} but only $\sim 13\,000$ cm^{-1} ($TcCl_6^{--}$) to $\sim 17\,000$ cm^{-1} ($ReCl_6^{--}$) above $\pi^{23}\gamma_5^4$. Actually, the strongest band of $\pi^{23}\gamma_5^3\gamma_3$ 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 $\sim 53\,000$ cm^{-1} in $ReCl_6^{--}$ outside of the region available here. By the same token, the similar excited level belonging to $\pi^{23}\gamma_5^4$ should occur at $\sim 36\,000$ cm^{-1}. This agrees well with the strongest maximum at 35 650 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 γ_4 among the twelve π 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 $\gamma_5^3 \rightarrow \gamma_5^2\gamma_3$ $^4\Gamma_5$ 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 (π even γ_4) $\rightarrow \gamma_5$ transition. We expect hence the strong (π odd γ_4) $\rightarrow \gamma_3$ 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 γ_j components (the first five seem to be even γ_7, even γ_8, odd γ_7, odd γ_8, and odd γ_8) of the π- or σ-vacancy multiplied by the numerous γ_5^4 levels. It is already evident [40] 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 Γ_7 and $d\,\Gamma_8$ though it is annoying that their wavenumbers are so close to 9 350 and 10 700 cm^{-1} characterizing [40] 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 $\pi^{23}\gamma_5^3\gamma_3$ 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.

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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 ε passes 1 000, it occurs at:

$$\begin{array}{llll} TcCl_6^{--}\ 25\,100; & TcBr_6^{--}\ 19\,100; & TcI_6^{--}\ 11\,700; & \\ ReCl_6^{--}\ 30\,000; & ReBr_6^{--}\ 22\,500; & ReI_6^{--}\ 13\,200. & (9) \end{array}$$

In order to get a quantitative measure of how much more oxidizing is Tc(IV) than Re(IV), we evaluate the *optical electronegativity*[2] x_{opt}. Table 4 corrects the wavenumber σ of the first intense band of the $\pi^{23}\gamma_5{}^4$ group with $2D$ from Table 2 in order to get σ_{corr} which defines for the central atom

$$\sigma_{corr} = (30\,000\ \text{cm}^{-1})\ [x_{opt}(X) - x_{opt}(M)] \quad (10)$$

	σ [cm^{-1}]	σ_{corr} [cm^{-1}]	x_{opt}	σ_{corr} (rel.) [cm^{-1}]	x_{opt} (rel.)
$TcCl_6^{--}$	29600	23200	2.23	25200	2.16
$TcBr_6^{--}$	22550	16450	2.25	18450	2.18
TcI_6^{--}	14000	8200	2.23	10200	2.16
$ReCl_6^{--}$	35650	29550	2.02	34000	1.86
$ReBr_6^{--}$	28400	22600	2.05	27100	1.89
ReI_6^{--}	15200	9600	2.18	14100	2.03

Table 4. Optical electronegativities of technetium(IV) and rhenium(IV).

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

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

though ReI_6^{--} presents a certain irregularity. This may be related to the interesting question[41] whether deviations occur from the normal, linear variation[42] of x_{opt} as function of q and oxidation number, when σ_{corr} tends towards zero.

Table 4 also corrects σ_{corr} from eq. (10) further to $\sigma_{corr(rel.)}$ by the relativistic effect $[2\,\zeta_{nd} - (\zeta_{nd}{}^2/35\,B)]$ in the central atom mentioned above. It may be noted that the difference between 4d³ and 5d³ is accentuated by this correction, whereas 4d⁴ and 5d⁴ would be brought closer. We remember, however, that x_{opt} of the ligands referring to the stabler π $(\omega = 1/2)$ electrons would be about 2.88 in Br and 2.67 in I, cancelling a part of the differences between the three heavy halogens.

Finally, Table 5 compares x_{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_{opt} of Mn(IV) would expected to be at least 2.5.

d^3		d^4		d^5	
Mo(III)	1.7			Ru(III)	2.1
Tc(IV)	2.25	Ru(IV)	2.4	Rh(IV)	2.6
				Os(III)	1.9
Re(IV)	2.05	Os(IV)	2.2	Ir(IV)	2.35
Ir(VI)	2.9	Pt(VI)	3.2		

Table 5. Optical electronegativities x_{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_{opt} derived from the electron transfer bands is 2.25 for Tc(IV) and 2.05 for Re(IV). Hence, the more oxidizing Tc(IV) is expected to have a sligtly greater tendency towards covalent bonding, and actually,

2. The nephelauxetic effect is slightly greater for the intra-sub-shell transitions of Tc(IV) than Re(IV). However, the influence of the ligands is far larger; the hexaiodides have a much smaller nephelauxetic ratio β_{55} than the hexafluorides. It may be mentioned that the influence of oxidation number is even more conspicuous than that of the ligands; IrF_6 has a smaller β_{55} than 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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led shell due to symmetry-restricted covalency] would be 2.5 for TcF_6^{--}, 1.5 for $TcCl_6^{--}$, 1.0 for TcI_6^{--}, 2.8 for ReF_6^{--}, 1.7 for $ReCl_6^{--}$, and 1.2 for IrF_6. Actually, there are good reasons to believe that the central field rather effects 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 Δ has been determined in TcF_6^{--} and ReF_6^{--}, showing the usual increase with principal quantum number (the two values are 1.31 and 1.51 times as large, respectively, as for MnF_6^{--}).

5. The blurring out of the vibrational structure suggests minor deviations from regular octahedral symmetry. These deviations were previously known [34] in K_2ReCl_6 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 RuF_6^-, the tetrameric [45] Ru_4F_{20}, and RhF_6 gas. These species are expected [35] 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 TcI_6^{--}; 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 oxo-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 $MoCl_6^{--}$ and $MoCl_6^-$ 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.

Acknowledgments

We would like to thank Professor W. HERR much for his kind encouragement of this work. Our thanks are due to Prof. F. FEHÉR, Institut für Anorganische Chemie der Universität Köln, who enabled us to use the Cary 14 spectrophotometer and to the German Federal Ministry for Scientific Research for the grant of the Zeiss spectrophotometer. Finally, we thank Dr. R. D. PEACOCK, who previously communicated to one of us a spectrum of ReF_6^{--} which, except for minor details, is similar to that reported here in the visible region.

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