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VIBRATIONAL SPECTRA AND FORCE CONSTANTS OF SOME OCTAHEDRAL
FLUORO- AND OXOFLUOROCOMPLEXES OF RHENIUM

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SUMMARY

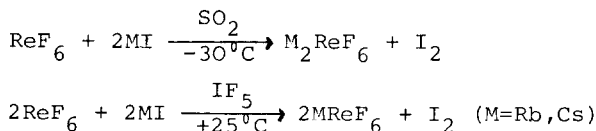
The vibrational spectra of the six-coordinated complexes $MReF_6$ ($M=No, K, Rb$) $MReOF_5$ ($M=Rb, Cs$), $KReO_2F_4$ and $K_2ReO_3F_3$ were recorded and assigned according to an octahedral arrangement of the ligands, giving O_h symmetry for the hexafluoro-anion, but only C_{4v} for the oxopentafluoro and C_{2v} both for the dioxotetrafluoro- and the trioxotrifluoro-complex, due to the arrangement of the different ligand atoms. From these frequency data, force constants of a MVFF were calculated. The values of the stretching force constants and the bonding in these compounds are discussed.

INTRODUCTION

So far, only very few publications dealt with the vibrational spectra of fluoro- and oxofluoro-compounds of rhenium. Thus, complete spectra were reported for ReF_7 , ReF_6 and ReF_6^{2-} [1-3], but only one infrared band is known for the rhenium (v)-complex ReF_6^- [4]. Of the oxofluoro-compounds, only the Raman spectrum of $ReOF_5^-$ in solution [5] and the vibrational spectra of the uncharged molecule $ReOF_5$ [6] were reported. A more extensive study of the vibrational spectra of such compounds seemed appropriate, as investigations on complexes of the sixth group transition metals Mo and W rendered interesting results [7,8], and similar aspects are expected for rhenium too.

EXPERIMENTAL

The alkali salts of the hexafluororhenate (V) have been prepared by reduction of ReF_6 with alkali iodide [9]. Using SO_2 at -30°C as a solvent, we got invariably M_2ReF_6 , even with an excess of ReF_6 , but in IF_5 at $+25^\circ\text{C}$, MReF_6 was formed:



The physical and chemical properties of our products are identical with those reported by Peacock [9].

NOReF_6 was reported by Bartlett et al. [10] without giving experimental details. We prepared the salt by condensing NO on solid ReF_6 . Even at liquid nitrogen temperature, the reaction $\text{NO} + \text{ReF}_6 \longrightarrow \text{NO}^+\text{ReF}_6^-$ started (indicated by the disappearance of the yellow colour of ReF_6) and it was brought to completeness by raising the temperature from -196° to $+20^\circ\text{C}$ removing excess NO.

KReO_2F_4 was prepared according to Peacock [11] and it was obtained as a purely white product (Peacock reported it as cream-coloured because of some included BrF_3).

The preparation of $\text{K}_2\text{ReO}_3\text{F}_3$ and MReOF_5 ($\text{M}=\text{Rb}, \text{Cs}$) was reported in the previous paper [12].

The Raman spectra of the crystalline powders were obtained with a Cary 82 spectrophotometer using the 488 nm argon laser line as exciting light. The infrared spectra were recorded as nujol mulls between CsI windows on Perkin-Elmer 577 and 325 instruments.

VIBRATIONAL SPECTRA

a) MReF_6 ($\text{M}=\text{NO}, \text{K}, \text{Rb}$)

For the hexafluoro-anion ReF_6^- 3 Raman ($A_{1g} + E_g + F_{2g}$) and 2 infrared (F_{1u}) bands not coinciding are observed according to the selection rules for O_h symmetry. All these modes are found for RbReF_6 and NOReF_6 with a complete identity of all wave numbers, but only the strongest bands (one Raman and one infrared) were

observed for $KReF_6$, somewhat shifted by the different cation. The weak additional infrared band at 265cm^{-1} indicates some lowering of symmetry, due to crystal effects. Assignment of the spectra poses no problem (Tab. 1).

TABLE 1

VIBRATIONAL SPECTRA OF $MReF_6$ ($M=NO, K, Rb$)

$KReF_6$		$RbReF_6$		$NOReF_6$		Assignment
IR	RA	IR	RA	IR	RA	
	703vs		701vs		701vs	$\nu_{ReF} (A_{1g})$
					639w	$\nu_{ReF} (E_g)$
612vs		612vs		612vs		$\nu_{ReF} (F_{1u})$
		265sh	255s	265sh	255s	$\delta_{ReF_6} (F_{2g})$
		241m		241m		$\delta_{ReF_6} (F_{1u})$

b) $MReOF_5$ ($M=Rb, Cs$)

Insertion of one oxygen atom instead of fluorine in the ligand octahedron, as in the case of $ReOF_5^-$ lowers the symmetry from O_h to C_{4v} , for which 11 Raman and 8 infrared bands are expected:

$$\Gamma_{C_{4v}} = 4A_1(RA+IR) + 2B_1(RA) + 1B_2(RA) + 4E(RA+IR).$$

All the infrared bands should occur in the Raman spectrum too. Indeed, 8 infrared bands are observed and 8 Raman lines (the remaining 3 being apparently too weak), most of them coinciding with infrared bands (Fig. 1). Assignment of the spectra for $ReOF_5^-$ is straightforward by comparison with $ReOF_5$ [6] and similar complexes of fifth, and sixth group transition metals [8,13]. The strong band at ca. 1000cm^{-1} is undoubtedly the ReO stretching vibration, those between 675 and 530cm^{-1} are the expected four ReF stretching vibrations, and the frequencies below 350cm^{-1} are the deformation modes (Tab. 2).

Of the ReF stretching vibrations, the lowest one belongs to the ReF bond opposite to ReO because of the well known: "trans" effect

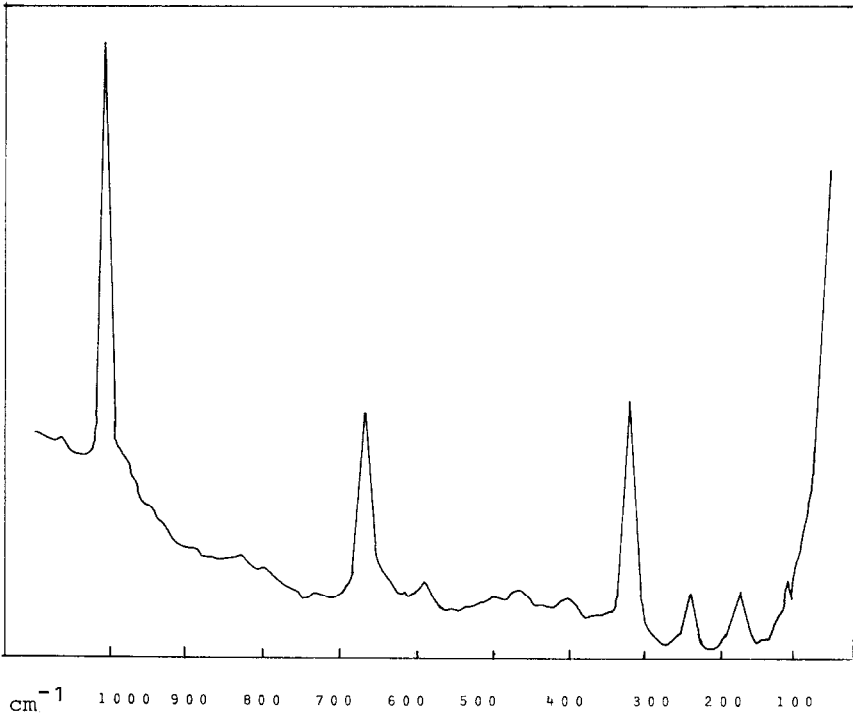


Fig. 1 a) Raman spectrum of CsReOF₅.

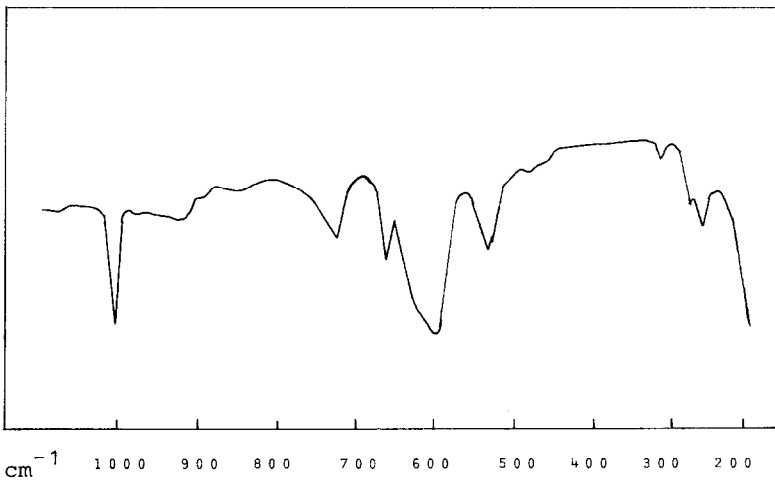


Fig. 1 b) Infrared spectrum of CsReOF₅.

TABLE 2

VIBRATIONAL SPECTRA OF $M\text{ReOF}_5$ ($M=\text{Rb}, \text{Cs}$)

RbReOF ₅		CsReOF ₅		ReOF ₅ ⁻ (sol.) [5]		ReOF ₅ [6]		Assignment (Symmetry C _{4v})
IR	RA	IR	RA	RA	IR	IR	RA	
1006s	1012vs	1002vs	1005vs	1008s,p	991s	991s	999s	ν ReO (A ₁)
671m	670s	662m	667s	736vs,p	738s	738s	738vs	ν ReF ₄ (A ₁)
608vs	612w	615vs	614vvw	700w,sh	713vs	713vs		ν ReF ₄ (E)
	572vvw		588w	590w			652m	ν ReF ₄ (B ₁)
532m	532vvw	535s		575w,p	643s		640m	ν ReF ₄ (A ₁)
318vw	324s	316w	324s	387s	365w		367s	δ OReF (E)
				370w			334s	δ ReF ₄ (B ₂)
278w		281m		330m,p	309s		309vw	δ ReF ₄ (A ₁)
260m		263s		298s	260s			δ ReF ₄ (E)
245vvw	245s		248s	233s				δ ReF ₄ (E)
	175w		176w					δ ReF ₄ (B ₁)

[14-17]: as it is much easier for the central metal atom, to obtain electrons from the oxygen tending to form multiple bonds than from the more electronegative and rigid fluorine, a very strong metal-oxygen bond with a high bond order will be formed at the cost of a very polar and rather weak metal-fluorine bond, if both compete. It should be noted, that ν_{ReO} has about the same frequency value for the complex as for ReOF_5 [6], but all ReF stretching vibrations have considerably lower wave numbers. This is to be expected and will be discussed later. ν_{ReO} agrees with the findings of Holloway and Raynor [5] too, but there are discrepancies for almost all other Raman lines, which cannot be entirely due to the different states and cations investigated. Thus, in the Raman spectrum observed by these authors, the upper two ReF stretching vibrations remain at values also found for ReOF_5 , whereas the other two are lowered to almost the same extent as observed by us, which seems rather unlikely. The larger number of Raman lines found by Holloway and Raynor indicates, that they might have had not pure ReOF_5^- , but a mixture of some compounds including ReOF_5^- .

c) KReO_2F_4

For ReO_2F_4^- , two arrangements of the oxygen ligands are possible either the two oxygen atoms are in trans-position and the ion has symmetry D_{4h} , or they are in cis position resulting in C_{2v} symmetry. The selection rules are rather different for these symmetry groups:

$$\Gamma_{D_{4h}} = 2A_{1g}(\text{RA}) + 2A_{2u}(\text{IR}) + 1B_{1g}(\text{RA}) + 1B_{2g}(\text{RA}) + 1B_{1u}(\text{inactive}) \\ + 1E(\text{RA}) + 3E_u(\text{IR})$$

$$\Gamma_{C_{2v}} = 6A_1(\text{RA+IR}) + 2A_2(\text{RA}) + 4B_1(\text{RA+IR}) + 3B_2(\text{RA+IR})$$

Thus, from the observed number of bands and their frequent coincidences in the Raman and infrared spectrum, C_{2v} symmetry with the oxygens in cis position is unambiguously confirmed for

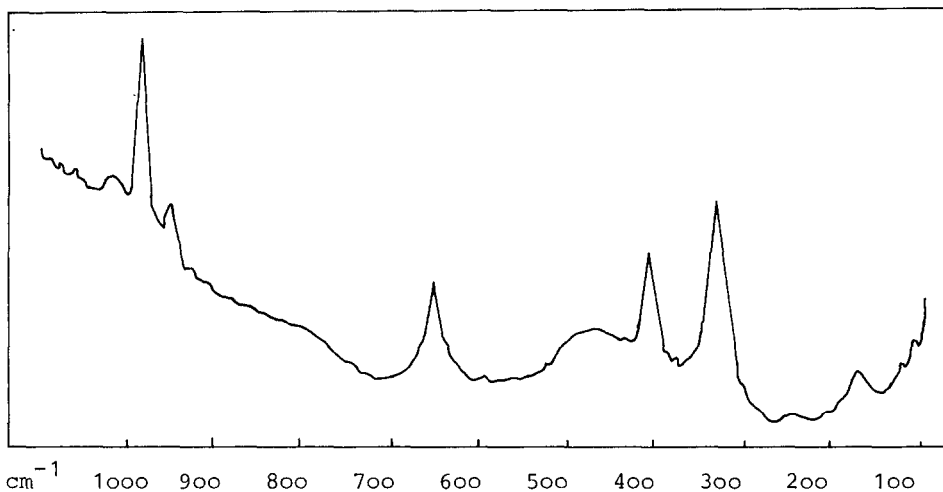


Fig. 2 a) Raman spectrum of KReO_2F_4

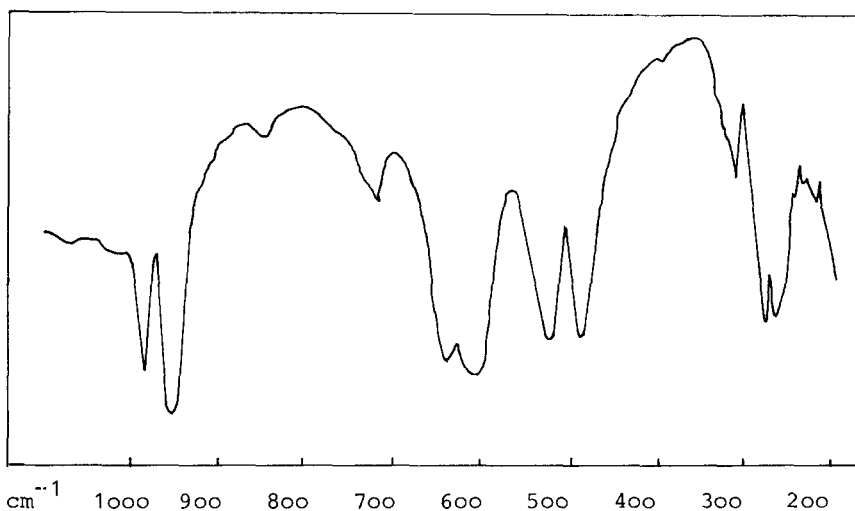


Fig. 2 b) Infrared spectrum of KReO_2F_4

ReO_2F_4^- (Fig. 3a). This is especially clear from the region of the stretching modes in the infrared spectrum, where 2 ReO and 4 ReF vibrations are observed, whereas only one of each kind should occur for D_{4h} symmetry (Fig. 2).

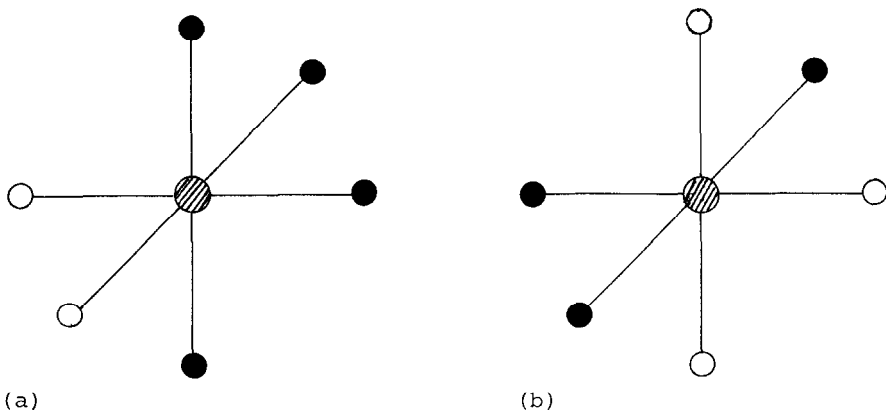


Fig. 3 Ligand arrangements for (a) ReO_2F_4^- , (b) $\text{ReO}_3\text{F}_3^{2-}$



Of the two ReO stretching vibrations, the higher one at 987 cm^{-1} can be assigned to the symmetric and the lower one at 951 cm^{-1} to the asymmetric mode, because the former is more intense in the Raman and the latter more intense in the infrared spectrum. For the ReF bonds, the trans-effect should be considered again. Therefore, the lower pair of frequencies (525 and 489 cm^{-1}) belongs to the bonds opposite to ReO, whereas the higher one (647 and 606 cm^{-1}) belongs to the linear ReF_2 group. For the latter pair, the band at 647 cm^{-1} can be assigned to the symmetric mode, that at 606 cm^{-1} to the asymmetric one because of the intensity relations. This assignment is more difficult for the lower pair of ReF stretching vibrations, which are of equal intensity in the infrared and both not observed in the Raman spectrum. However, from the value of the coupling constant obtained by a force constant calculation (see below) we suggest the higher frequency to be the symmetric mode again. Assignment of the 9 deformation vibrations must remain tentative, because no Raman polarization measurements were possible, which would have located at least the 3 deformation modes of species A_1 . Thus, the only assumption which was used and seems meaningful, is $\delta_{\text{ReO}_2} > \delta_{\text{OReF}} > \delta_{\text{ReF}_2}$ (Tab. 3).

TABLE 3

VIBRATIONAL SPECTRA OF KReO_2F_4

IR	RA	Assignment (Symmetry C_{2v})
987s	987s	$\nu_{\text{ReO}}(A_1)$
951vs	951w	$\nu_{\text{ReO}}(B_1)$
645s	649m	$\nu_{\text{ReF}}(A_1)$
606vs	606vvw	$\nu_{\text{ReF}}(B_2)$
525s		$\nu_{\text{ReF}'}(A_1)$
489s		$\nu_{\text{ReF}'}(B_1)$
	410m	$\tau_{\text{ReO}_2}(A_2)$
319m	325s	$\delta_{\text{ReO}_2}(A_1)$
278m		$\gamma_{\text{ReO}_2}(B_2)$
266m		$\delta_{\text{OReF}}(B_1)$
221vw		$\delta_{\text{ReF}_2}(A_1)$
	180w	$\delta_{\text{ReF}_2'}(A_1)$
	140vw	$\gamma_{\text{ReF}_2}(B_2)$
	115vvw	$\tau_{\text{ReF}_2}(A_2)$

($\delta_{\text{ReF}_2'}(B_2)$ was estimated as 155 cm^{-1} for the calculation of force constants)

d) $\text{K}_2\text{ReO}_3\text{F}_3$

Again, two structural alternatives are possible for $\text{ReO}_3\text{F}_3^{2-}$: either the three oxygens are in one plane, and the three fluorine atoms in another one, perpendicular to the oxygen plane, giving C_{2v} symmetry for the ion, or the ligands form an all-cis-configuration, resulting in C_{3v} symmetry. The selection rules of both symmetry groups for $\text{ReO}_3\text{F}_3^{2-}$ are:

$$\Gamma_{C_{3v}} = 4A_1(\text{Ra+IR}) + 1A_2(\text{RA}) + 5E(\text{RA+IR})$$

$$\Gamma_{C_{2v}} = 6A_1(\text{RA+IR}) + 1A_2(\text{RA}) + 4B_1(\text{RA+IR}) + 4B_2(\text{RA+IR})$$

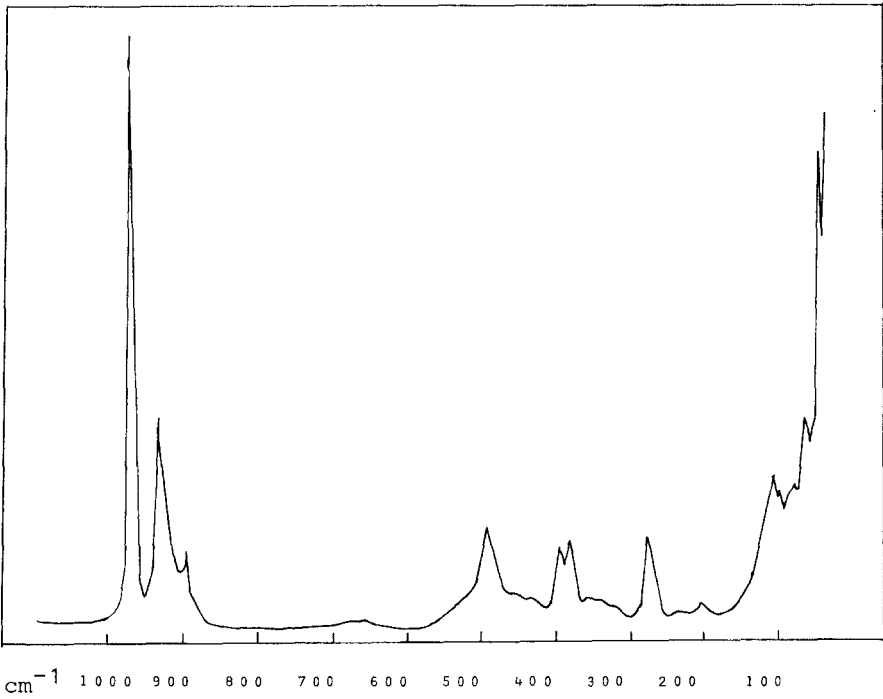


Fig. 4 a) Raman spectrum of $K_2ReO_3F_3$

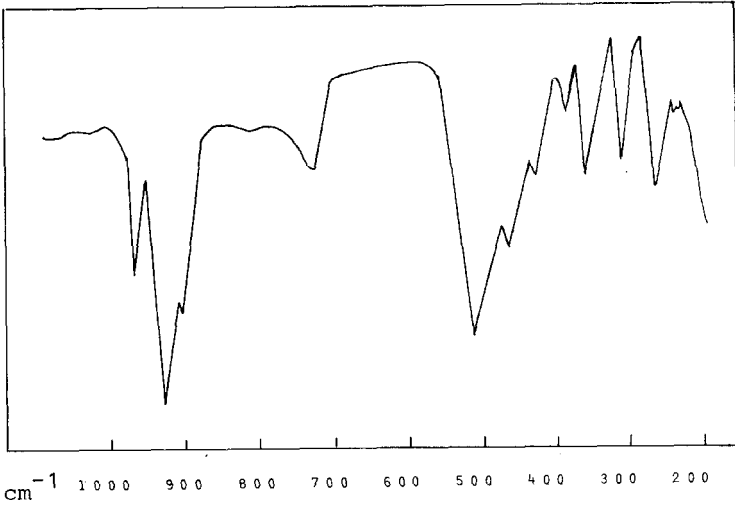


Fig. 4 b) Infrared spectrum of $K_2ReO_3F_3$

The total of 15 frequencies found altogether in the Raman and infrared spectra favours symmetry C_{2v} , and this is especially confirmed by the findings in the region of the stretching vibrations, where 3 ReO and 3 ReF modes are observed. This is in agreement with the expectation for C_{2v} , while only 2 vibrations of each type should occur for symmetry C_{3v} (Fig. 3b and 4).

Despite this easy identification of the overall structure of the ion, a detailed assignment remains difficult because of the lack of Raman polarization data. For the proposed structure, the linear ReL_2 groups ($L=O$ or F) should each give rise to two stretching vibrations: a symmetric (species A_1) and an asymmetric one (species B_1 or 2). The ReO and ReF bonds opposite to one another should produce both one additional A_1 mode. Unfortunately, the normal intensity relations (Symmetric stretching vibrations more intense in the Raman spectrum, asymmetric ones in the infrared) do not hold for $ReO_3F_3^{2-}$, except for the highest ReO frequency at 969 cm^{-1} , which can be unequivocally assigned to an A_1 mode. But otherwise, strong (respectively weak) bands both in the Raman and infrared spectrum coincide.

However, if one considers the validity of the trans-effect for $ReO_3F_3^{2-}$ too, the ReF bond opposite to ReO should be weaker than the other two and its vibration should be assigned to the lowest frequency, observed (430 cm^{-1}) in the ReF stretching region. Extending the concept of the trans-effect also to the ReO bands, one might assume, that for the linear ReO_2 group the bond orders should be lower than for ReO opposite to ReF, because the same d-orbitals of the central atom must be used by the electrons of the colinear multiple bonds. Thus, the highest ReO frequency (969 cm^{-1}) observed should belong to the bond opposite to ReF. This would leave the bands at 928 and 902 cm^{-1} for the linear ReO_2 group, and 504 and 466 cm^{-1} for the linear ReF_2 group. Which of these are the symmetric and asymmetric modes, cannot be decided without polarization measurements, but from the values of the coupling constants obtained by a force constant calculation (see below) we would tend to prefer an assignment of the higher frequencies to the symmetric modes both for ReO_2 and ReF_2 . - The deformation vibrations were assigned tentatively, taking into account the rule $\delta_{ReO_2} > \delta_{OReF} > \delta_{ReF_2}$ again.

TABLE 4

VIBRATIONAL SPECTRA OF $K_2ReO_3F_3$

IR	RA	Assignment (Symmetry C_{2v})
969s	969s	ν_{ReO} (A ₁)
926vs	930s	ν_{ReO} (A ₁)
905w	899m	ν_{ReO} (B ₁)
510vs	498m	ν_{ReF} (A ₁)
466m		ν_{ReF} (B ₂)
430m		ν_{ReF} (A ₁)
387w	391w	δ_{ReO_2} (B ₂)
	382w	δ_{ReO_2} (A ₁)
368s		$\delta_{O'ReF}$ (B ₁)
312s		δ_{OReF} (B ₂)
266s	264m	δ_{OReF} (B ₁)
	231vw	δ_{OReF} (B ₂)
	201vw	δ_{ReF_2} (B ₁)
	150vvw	τ_{OReF} (A ₂)
	112m	δ_{ReF_2} (A ₁)

CALCULATION OF FORCE CONSTANTS

From the frequency data of ReF_6^- , $ReOF_5^-$, $ReOF_5$ (from [6]), $ReO_2F_4^-$ and $ReO_3F_3^{2-}$, force constants were calculated, always assuming a regular octahedral arrangement of the ligands, with a symmetry according to the spectroscopic findings, and using a MVFF neglecting all off-diagonal interaction constants in the symmetry coordinate space. This approximation should be valid, as

the mass of the central atom compared with the ligands' masses is so large, that there is almost no interaction and all the modes are quite characteristic [18]. For the same reason, the uncertainty in assigning the deformation vibrations does not influence the values of the stretching force constants, which will be solely discussed.

The stretching force constants calculated in this way, are given in Tab. 5 together with the stretch/stretch interactions between similar bonds. Because of these data, we prefer set I (together with the corresponding assignment) both for ReO_2F_4^- and $\text{ReO}_3\text{F}_3^{2-}$.

DISCUSSION

Following the assignments discussed earlier, the force constants for ReF bonds opposite to ReO are smaller than those opposite to ReF, and are in accord with the trans-effect. The most striking phenomenon is the sharp decrease of the ReF stretching force constants when either the oxidation state of the central atom decreases or fluorine ligands are replaced by oxygen. To show this more clearly, all known stretching force constants of octahedral fluorocompounds of rhenium are arranged in Tab. 6 to meet these trends. For the oxofluorocompounds, mean values are given if more than one force constant value occurs for one type of bond.

The decrease of the ReF stretching force constants is due to an increase of the polarity of the ReF bonds [21]. This change of bond polarity may have different reasons.

In both series, the decrease of the ReF stretching force constants is correlated to an increase of the negative charge of the complex. This negative charge will be mainly localized at the fluorine atoms, thus making the bonds more polar [22]. An additional weakening of the bonds may be caused by the increasing mutual repulsion of the negative F ligands itself. Concerning the influence of the oxidation state, its decrease will lower the electronegativity of the central atom and thus its polarizing effect on the electrons of the fluorine ligands. An additional effect may be exerted by the increasing occupation of the d-orbitals of the central atom itself, however, a more extensive study of octahedral

TABLE 5
STRETCHING FORCE CONSTANTS CALCULATED FOR ReF_6^- , ReOF_5^- , ReO_2F_4^- , $\text{ReO}_2\text{F}_3^{2-}$ AND $\text{ReO}_3\text{F}_3^{2-}$
(in $\text{mdyn}\text{Å}^{-1} = 10^2\text{Nm}^{-1}$)

	$F_{O/F}$	$F_{O/O}$	f_{OO}^+ (cis)	f_{OO}^- (trans)	$F_{F/O}$	$F_{F/F}$	f_{FF}^+ (cis)	f_{FF}^- (trans)
ReF_6^-						4.17	0.15	0.72
ReOF_5^-	8.85			2.88		3.86	0.34	0.49
ReOF_5	8.51			4.16		5.09	0.33	0.34
ReO_2F_4^- (I)	8.15		0.30	2.61		4.06	0.19	0.65
ReO_2F_4^- (II)	8.12		0.31	2.63		4.05	-0.19	0.66
$\text{ReO}_3\text{F}_3^{2-}$ (I)	8.10	7.32		1.81		2.41		0.42
$\text{ReO}_3\text{F}_3^{2-}$ (II)	8.10	7.29		1.81		2.38		0.05

	Stretching force constants	Interaction constants
$F_{O/F}$	ReO bond opposite to ReF	f_{OO} (cis): between 2ReO bonds (90°)
$F_{O/O}$	ReO bond opposite to ReO	f_{OO} (trans): between 2ReO bonds (180°)
$F_{F/O}$	ReF bond opposite to ReO	f_{FF} (cis): between 2ReF bonds (90°)
$F_{F/F}$	ReF bond opposite to ReF	f_{FF} (trans): between 2ReF bonds (180°)

Assignments: (in cm^{-1})	ReO_2F_4^- (set I):	$525(A_1)$, $489(B_1)$
	ReO_2F_4^- (set II):	$525(B_1)$, $489(A_1)$
	$\text{ReO}_3\text{F}_3^{2-}$ (set I):	$928(A_1)$, $902(B_1)$, $503(A_1)$, $466(B_2)$
	$\text{ReO}_3\text{F}_3^{2-}$ (set II):	$928(B_1)$, $902(A_1)$, $503(B_2)$, $466(A_1)$

TABLE 6

COMPARISON OF STRETCHING FORCE CONSTANTS FOR RHENIUM-FLUORO-COMPLEXES
(in $\text{mdyn}\text{\AA}^{-1} = 10^2 \text{Nm}^{-1}$)

	ReF ₆	ReOF ₅	ReO ₂ F ₄	ReO ₃ F ₃
Re (VII) f_{ReF}	6.00 [19]	4.90	3.34	2.21
f_{ReO}		8.51	8.15	7.58
Re (VI) f_{ReF}	5.18 [20]	3.66		
f_{ReO}		8.85		
Re (V) f_{ReF}	4.17			
Re (IV) f_{ReF}	2.76 [3]			

If there are more than one force constant value for one type of bond (e. g. Re-O or Re-F), mean values are given.

transition metal fluoro complexes reveals, that this is of minor importance [23]. For the oxofluoro complexes, besides the increase of the negative complex charge, successive replacement of fluorine by the less electronegative oxygen causes a reduction of the inductive effect of the ligands on the central atom and therefore a decrease of its electronegativity. Moreover, the oxygens are able to form multiple bonds, at the expense of the very polar ReF bonds. This is not only true for the ReF bonds opposite to ReO ("trans-effect"), but also - though to a lesser extent - for all other ReF bonds. The preference for multiple bonds with a maximum bond order in combination with very polar bonds to fluorine is not only found for transition metal complexes, but for all cases, where ligands apt to form multiple bonds and fluorine atoms are present at the same time (e.g. ONF, ONF₃ contrary to ONR₃; FOOF and FSSF contrary to the corresponding hydrogen compounds, NSF and NSF₃) [24]. For the oxofluoro complexes of rhenium, the high force constant values obtained for ReO show this multiple bond character too. It should be noted, that the strength of the ReO bond is almost unaffected by a change of oxidation state (ReOF₅⁻ and ReOF₅), in contrast to the ReF bonds. If the number of oxygen ligands is increased, there is some reduction of the ReO force constants (but less than ReF!) which is due to the accumulation of multiple bonds. All these results are in complete agreement with similar findings for other transition metal fluoro-complexes [7,8,25,26].

Finally, it should be mentioned, that complex formation will be limited or even prevented if the bonds to fluorine would become too polar. This may be true, if both effects occur together, i.e. for complexes, in low oxidation states with high oxygen content. Thus we have not been able as yet to get the rhenium compounds ReO₂F₄²⁻, ReO₃F₃³⁻ and ReOF₅²⁻

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