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Low Temperature Absorption Spectra of TcO_4^- and ReO_4^- in $KClO_4$

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The low temperature spectra of TcO_4^- and ReO_4^- both show two band systems with pronounced vibrational structures. The bands are identified as ${}^1A_1 \rightarrow {}^1T_2$ transitions. No other bands are observed with certainty. It seems likely that the $KClO_4$ crystals contain $KReO_4$ crystallites. They are therefore not pure mixed crystals. It is concluded that the virtual orbital ($2e$) used in the construction of the low lying states resembles an atomic nd orbital more and more when going from $n = 3$, Mn to $n = 5$, Re.

Die Tieftemperaturspektren von TcO_4^- und ReO_4^- zeigen beide zwei Bandensysteme mit ausgeprägten Schwingungsstrukturen. Die Banden werden als ${}^1A_1 \rightarrow {}^1T_2$-Übergänge identifiziert. Keine anderen Banden werden mit Sicherheit beobachtet. Es scheint wahrscheinlich, daß die $KClO_4$-Kristalle $KReO_4$-Kristallite enthalten und deswegen keine reinen Mischkristalle sind. Es wird geschlossen, daß das virtuelle Orbital ($2e$), welches zur Konstruktion der tiefliegenden Zustände gebraucht wird, in der Reihe $n = 3$, Mn bis $n = 5$, Re immer weitgehender einem nd-Atomorbital ähnelt.

Introduction

In view of the continued interest in the electronic absorption spectra of tetrahedrally coordinated d^0 transition metal ions it seemed natural to study the low temperature spectra of TcO_4^- and ReO_4^-. The solution spectra of these ions have recently been reported [1], but it was anticipated that more detail would emerge by recording the spectra of single crystals at low temperatures. As a result, we can now offer a somewhat better analysis of the vibrational band structures than was previously possible. Some conjectures regarding the non-appearance in these ions of the so-called "Teltow band" have also been made.

Experimental

$KClO_4$ crystals containing 0.5, 1.5, and 3 mol-% respectively of TcO_4^- were prepared by the following procedure: a 0.1 M solution of ammonia in water was saturated with $KClO_4$(BDH) at 60° C, and an appropriate amount of a 0.26 M solution of $NH_4Tc^{99}O_4$ (Amersham Radiochemical Centre, England) in 0.1 M ammonia was added. The container was then tightly closed and placed in a thermostat the temperature of which was set to decrease at 2° C per day for 25 days. Plate-shaped crystals were individually picked out of the solution and used for the measurements.

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For the $KClO_4$ crystals doped with ReO_4^- the same procedure was employed. Aqueous solutions of $KReO_4$ (purity $\geqq 99.9\%$, Koch Light Laboratories Ltd.) and $KClO_4$ with perrhenate contents ranging from 0.5–4.0 mol-% were used.

Absorption spectra were measured at temperatures between 2.5° K and 77° K using both a Cary 14 spectrometer (dispersion 32 – 12 Å/mm) and a Zeiss 2 m grating spectrograph (dispersion 8 Å/mm). The Zeiss spectra were recorded on Kodak 103-F and SWR films. For the spectra measured between 2.5 and 4.2° K an immersion dewar with a device to pump on the liquid helium was employed. The spectra between 4.2 and 77° K were obtained using a helium gas-flow dewar. The cryostat described by Morris *et al.* [2] was modified for spectroscopic use.

For the experiments with polarized radiation the crystals were oriented using X-ray diffraction photographs taken with a Buerger precession camera. The incident light beam was always parallel to the *a* axis of the $KClO_4$ host crystal, with the electric vector either parallel to *b* or to *c* using the setting of the crystallographic axes given by Donnay [3]. Glan-Thompson prisms were used to polarize the light.

General Features of the Absorption Spectra

As has already been observed in the solution spectra [1] of TcO_4^- and ReO_4^- the main feature of the absorption spectra in the UV region are two strong, overlapping band systems. We shall call the lower and higher energy systems band system I and II respectively. In the crystal spectra of both compounds both band systems exhibit vibrational structure. Due to the overlap, only an estimate of the origin of system II can be made. On the high energy side of system II in

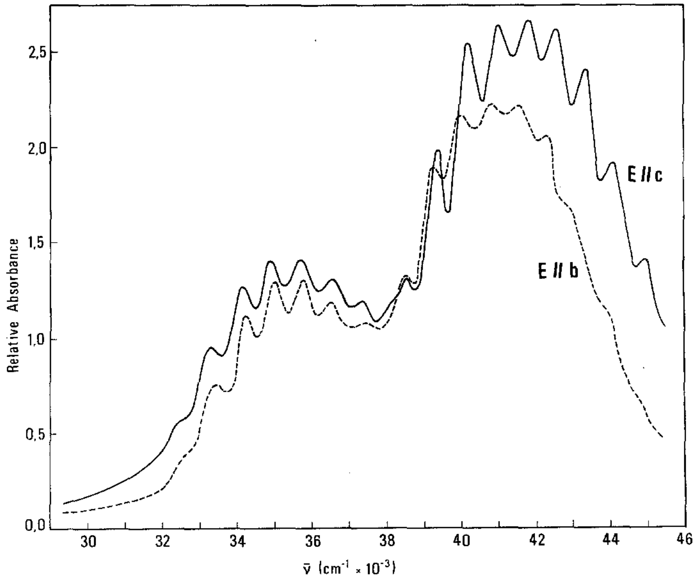

Fig. 1. UV absorption spectrum of TcO_4^- in a $KClO_4$ host lattice at liquid helium temperature

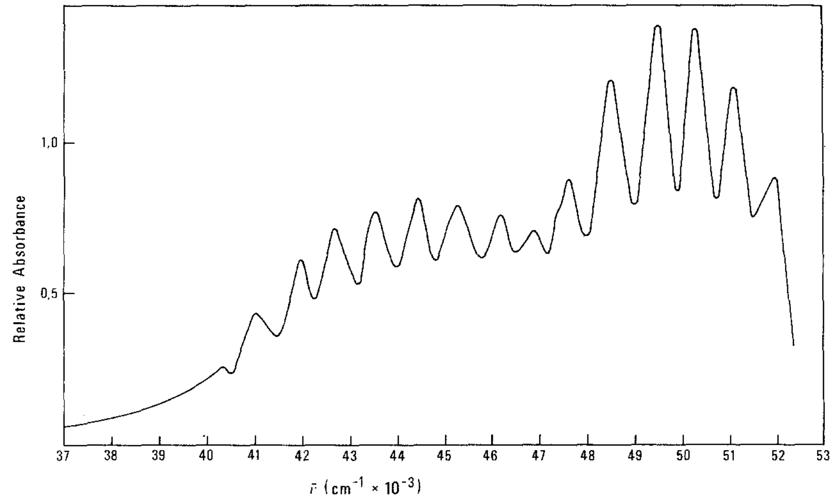

Fig. 2. UV absorption spectrum of ReO_4^- in a $KClO_4$ host lattice at liquid helium temperature

TcO_4^- the absorbance increases slightly without, however, reaching a maximum in the wavelength region covered in this study. On the low energy side of system I both TcO_4^- (Fig. 1) and ReO_4^- (Fig. 2) show very weak, broad and structureless absorption.

The region on the low energy side of band systems I has been examined very carefully (2 m Zeiss, resolution ~1 Å/mm; temperature 2.5° K; "concentration" of the crystals up to 4 mol-%, in both compounds). No sharp absorption lines comparable to those observed in permanganate crystal spectra [4–6] could be found between 32000 cm^{-1} and 25000 cm^{-1} in TcO_4^- and between 40000 cm^{-1} and 30000 cm^{-1} in ReO_4^-. There seems to be, however, structureless broad absorption, best seen in Cary spectra, in the ascent to the first component of the band systems I.

Analysis of the TcO_4 Spectra

Band System I

Progressions in 795 cm^{-1} and 806 cm^{-1} are observed $\|$ and $\perp$ (with the electric vector parallel and perpendicular) respectively to the symmetry plane of the site group C_s. The vibrations responsible for these progressions are undoubtedly totally symmetric vibrations ν_1 of the pertechnetate ion in the excited states. ν_1 for a regular tetrahedral TcO_4^- ion in the ground state [7] is 912 cm^{-1}. It is thus diminished by 11.6–12.8% in the excited state, compared to 9.1% in the corresponding state of MnO_4^-.

The values given in Table 1 for the origins, 32677 cm^{-1} $\|$ and 32576 cm^{-1} $\perp$, are not very accurate because they occur only as shoulders. Based on the most intense "components" 3, 4, and 5, a splitting $E\| - E\perp$ of about 70 cm^{-1} between the absorption maxima of the spectra in the two polarization directions can be measured. The corresponding value for MnO_4^- in the same host lattice is [4] some 20 cm^{-1}.

Table 1. Vibrational structure in the absorption spectrum of TcO_4^- dissolved in $KClO_4$

$\parallel b$ ("Crystal Data" setting) ($E \parallel$ to the symmetry plane of the site group C_s)		$\parallel c$ ("Crystal Data" setting) ($E \perp$ to the symmetry plane of the site group C_s)	
Positions of Maxima (cm^{-1})	Δ	Positions of Maxima (cm^{-1})	Δ
Band system I			
32677 sh	0	32576 sh	0
33435	(758)	33372	(796)
34237	802	34159	787
35020	783	34944	785
35804	784	35751	807
36561	757	36593	842
37408	847	37402	809
		38334 sh	(932)
Average	795	Average	806
Band system II			
38544 sh	0	38619	0
39254	(710)	39432	813
40023	769	40234	802
40823	800	41062	828
41599	776	41846	784
42364	765	42614	768
43135	771	43400	786
43885	750	44150	750
		44951	801
		45756 sh	(805)
		46624 sh	(868)
Average	772	Average	791

Band System II

Progressions in 772 cm^{-1} and 791 cm^{-1} are observed $\parallel$ and $\perp$ respectively. These values indicate a decrease of ν_1 by 15.3% ($\parallel$) and 13.3% ($\perp$) respectively compared to the ground state of pertechnetate. The components in the $\parallel$ spectrum are somewhat broader than the corresponding bands in the $\perp$ spectrum. This probably indicates that each $\parallel$ component is composed of at least two unresolved peaks. With a site group of C_s for the TcO_4^- ions in the $KClO_4$ crystal two origins are expected in the spectrum measured with the electric vector perpendicular to the z axis. The progression frequencies are 15–23 cm^{-1} smaller than in the first band system, compared to 18 cm^{-1} and 20 cm^{-1} in the spectra of permanganate and perrhenate respectively. The differences of the positions of the absorption maxima in the two polarization directions, $E\parallel - E\perp$, indicate a large site group splitting. For the most intense components the average splitting is -253 cm^{-1}, much larger and of opposite sign to that in the first band system. Splittings of this order of magnitude have not been observed in diluted $KMnO_4/KClO_4$ crystals, but have been recorded in diluted $LiMnO_4 \cdot 3H_2O/LiClO_4 \cdot 3H_2O$ and in $Ba(MnO_4)_2 \cdot 3H_2O/Ba(ClO_4)_2 \cdot 3H_2O$ crystals [8, 9].

Table 2. Vibrational structure in the absorption spectrum of $KReO_4/KClO_4$ crystals

Positions of Maxima (cm^{-1})	Δ
Band system I	
40066	0
40933	867
41795	862
42630	835
43461	831
44315	854
45155	840
46018 sh	(863)
Average	848
Band system II	
45934 sh	0
46775	(841)
47393 sh	(618)
47582	807 (189)
48237 sh	(655)
48418	836 (181)
49227	809
50052	825
50878	826
51685	807
Average	818

The different behaviour of MnO_4^- and TcO_4^- ions in a $KClO_4$ host lattice is understandable when the M–O distances are compared: Cl–O = 1.46 Å, Mn–O = 1.63 Å, Tc–O = 1.73 Å. The latter value has not been experimentally determined but can be reasonably estimated [10]. While $KClO_4$ and $KMnO_4$ are isomorphous and orthorhombic, $KTcO_4$ (as well as $KReO_4$) crystallizes with a tetragonal scheelite structure [11].

Therefore, the environmental forces acting on a pertechnetate ion "dissolved" in a potassium perchlorate lattice are certainly greater than in diluted $KMnO_4/KClO_4$ crystals and can well be responsible for the observed large site splitting.

Analysis of the ReO_4^- Spectrum

Band System I

A regular progression in 848 cm^{-1} is built upon the origin at 40066 cm^{-1}. Since the totally symmetric vibration of regularly tetrahedral ReO_4^- in the ground state [7] is 971 cm^{-1} the decrease in frequency in going to the excited state is thus 12.7%. Attempts were made to record spectra with polarized radiation. However, due to experimental limitations this was only possible for the first five "components". The positions of the absorption maxima were the same with both polarizations. This might mean that the site group splitting is too small to be detected. However, remembering that the splitting was larger in pertechnetate than in permanganate and noting that the Re–O distance [10] is 1.76 Å it seems more probable that we are not dealing with mixed crystals but with $KClO_4$ crystals containing $KReO_4$ crystallites. In other words, what has effectively been measured is a powder spectrum of potassium perrhenate in a matrix of potassium perchlorate.

Band System II

The overlap with band system I is very great and the assignment of the components in the overlap region is difficult. The third and fourth components attributed to band system II each have a shoulder on the low energy side that is certainly genuine and which probably has nothing to do with the overlapping band system I. The average spacing between the absorption maxima is 818 cm^{-1}, 30 cm^{-1} smaller than in the first band system and 15.8% smaller than ν_1 in the ground state of perrhenate.

There are possibly more components of this band system beyond our experimental limit of 52000 cm^{-1}.

Comparison of the Band Systems I of MnO_4^-, TcO_4^-, ReO_4^-

In the first strong band system of the permanganate crystal spectra a great deal of fine structure can be resolved. However, the spectra of TcO_4^- and ReO_4^- in $KClO_4$ exhibit only one progression in each case. The half widths of the "components" of these progressions are ~600 cm^{-1} for both compounds, compared to 200–300 cm^{-1} in the permanganate under similar experimental conditions.

A second striking observation is the relative intensities of the "components" of each progression. We observe a shift of maximum intensity towards higher components in the sequence MnO_4^-, TcO_4^-, ReO_4^-.

Discussion

The calculations of Dahl and Johansen [12] indicate that in permanganate the two low-lying absorption bands with pronounced vibrational structure are to be assigned [8, 9] as ${}^1A_1 \to {}^1T_2(t_1 \to 2e)$ and ${}^1A_1 \to {}^1T_2(3t_2 \to 2e)$. The two ${}^1T_2$ states are of course mixed, and also contain admixtures of higher lying ${}^1T_2$ states. In T_d symmetry electric dipole transitions are allowed only to the ${}^1T_2$ states. Both of the electronic excitations $(t_1 \to 2e)$ and $(3t_2 \to 2e)$ will also produce ${}^1T_1$ states. These are placed on the red side of the ${}^1T_2$ states [5, 6], and the first ${}^1T_1$ is responsible for the "Teltow band" found in the MnO_4^- and $CrO_4^=$ ions.

Calculations by Ziegler [13] show the $3t_2$ orbital to be a nearly-pure ligand orbital in MnO_4^-, TcO_4^-, and ReO_4^-; by symmetry the t_1 orbital is a pure ligand orbital. On the other hand the $2e$ orbital is given by a mixture $\psi(2e) = \alpha(d_e) + \beta(\Sigma$ ligand orbitals). In the INDO approximation scheme the separation $E({}^1T_2) - E({}^1T_1)$ will therefore be proportional to β^2, and the same will be the case for the interaction term between the two ${}^1T_2$ states and the two ${}^1T_1$ states. To a first approximation we can therefore assume that the smaller the value of β, the closer can the states approach each other and the smaller will the energy separation be between the "Teltow band" and the first structured allowed

${}^1A_1 \rightarrow {}^1T_2$ transition. Indeed, for $\beta = 0$, the ${}^1A_1 \rightarrow {}^1T_1$ transition is calculated to lie on the blue side of the ${}^1A_1 \rightarrow {}^1T_2$ transition [5].

The mixing parameter β is expected to decrease through the series MnO_4^-, TcO_4^-, and ReO_4^-, since the energy separations between the oxygen ligand orbitals and the metal nd-orbitals, $n = 3$, 4, and 5, become larger. Consequently in ReO_4^-, $\psi(2e)$ is expected to be nearly pure $5d_e$, and both the allowed transitions ${}^1A_1 \rightarrow {}^1T_2(1)$ and ${}^1A_1 \rightarrow {}^1T_2(2)$ should be found close together possessing identical band shapes. This is indeed what is observed experimentally. The absence of a "Teltow band" is also explained, since we should expect it to be hidden under the first strong ${}^1A_1 \rightarrow {}^1T_2$ transition.

The spectrum of TcO_4^- is intermediate between the spectrum of MnO_4^- and ReO_4^-. Again the appearance of the "Teltow band" is probably obscured by the first strong transition. Furthermore, from an overall examination of the absorption spectrum it seems as if the characteristics of the first permanganate band are mirrored in the second pertechnetate band and those of the second permangante band in the first pertechnetate band. Evidently the potential surface of the ${}^1T_2(1)$ state found in MnO_4^- is closer to the second ${}^1T_2$ potential surface of TcO_4^- than it is to the first.

In both TcO_4^- and ReO_4^- the spectral measurements reveal a tail stretching towards the red at the bottom of the first ${}^1A_1 \rightarrow {}^1T_2$ band. We take this to indicate the presence of some spin forbidden, $S = 0 \rightarrow 1$, transitions. Such transitions are expected [14] on the red side of ${}^1A_1 \rightarrow {}^1T_2(1)$, and the high value of the spin-orbit coupling constant in ReO_4^- should certainly make them more pronounced here than in, say, MnO_4^-. Since, however, we can observe no spectral details, we offer no further comment on this aspect.

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