Resonance Raman Studies of the Peroxotitanate(IV) Complexes $K_2(Ti(O_2)(SO_4)_2)\cdot 5H_2O$ and $K_2(Ti(O_2)(C_2O_4)_2)\cdot 3H_2O$

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Abstract

The resonance Raman spectra of $K_2(Ti(O_2)(SO_4)_2)\cdot 5H_2O$ and $K_2(Ti(O_2)(C_2O_4)_2)\cdot 3H_2O$ are recorded. The results are consistent with the triangular structure of the peroxotitanium unit, $Ti(O_2)$, with C_{2v} symmetry. The ν(O–O), ν_s(Ti–O) and ν_{as}(Ti–O) are observed around 890, 610 and 535 cm^{-1}, respectively. The resonance effects are shown to be associated with the 425 nm absorption band. This band is assigned to the $O_2^{2-} \rightarrow Ti(IV)$ charge-transfer transition. The calculated force constant values for the O_2^{2-} and Ti–O bonds are 320 and 275 N m^{-1}, respectively.

Introduction

The reaction between Ti(IV) and H_2O_2 was first recognized in 1870 by Schönn [1]. It produces an intense orange color and therefore the reaction has been served extensively as a sensitive test for the detection of titanium(IV) or hydrogen peroxide. The above reaction can also take place in the presence of various complexing agents such as fluoride, sulphate, oxalate, dipicolinate and EDTA and the corresponding peroxotitanium complexes have been isolated [2–8]. In all of these complexes the Ti(IV) to O_2^{2-} ratio is 1:1 where the peroxo group acts as a bidentate ligand coordinated either to the same Ti(IV) ion forming the triangular $Ti(O_2)$ unit or coordinated to two Ti(IV) ions as a bridging group. This is dependent upon the pH value of the reaction media as well as the nature of the complexing agent [8, 9].

Many infrared studies on the peroxotitanium complexes under investigation $K_2(Ti(O_2)(SO_4)_2)\cdot 5H_2O$ and $K_2(Ti(O_2)(C_2O_4)_2)\cdot 3H_2O$ are reported in the literature and a wide disagreement is found between them [5, 10–13]. No Raman data is available in the literature for these solid complexes. Both complexes absorb in the visible at 425 nm. Such absorption arises from the charge-transfer transition of the type $O_2^{2-} \rightarrow Ti(IV)$. In previous work the resonance Raman method was successfully used in characterizing the metal–peroxo part in short-lived as well as stable compounds [14–16] using excitation wavelength coincident or close to the $O_2^{2-} \rightarrow$ metal cation, electronic transition.

The purpose of the work reported here is to employ the resonance Raman technique to characterize the vibrational bands for $K_2(Ti(O_2)(SO_4)_2)\cdot 5H_2O$ and $K_2(Ti(O_2)(C_2O_4)_2)\cdot 3H_2O$. These enable an assessment of the type of structure and bonding characters particularly concerning the $Ti(O_2)$ part of these molecules. Normal coordinate treatment is included.

Experimental

Preparation of Samples

The peroxodisulphatotitanate(IV), $K_2(Ti(O_2)(SO_4)_2)\cdot 5H_2O$ was prepared according to the method described by Schwarz and Giese [4]. The preparation of the peroxodioxalatotitanate(IV), $K_2(Ti(O_2)(C_2O_4)_2)\cdot 3H_2O$ was carried out by the method of Griffith [5]. The composition of each compound was found to correspond closely to the literature value. Compounds were kept over P_2O_5 in a desiccator to prevent decomposition.

Spectroscopic Measurements

Raman spectra of both peroxo compounds were obtained using a Cary Model 82 spectrometer and a Coherent Radiation Innova 12 argon ion laser. In order to prevent the photochemical and thermal decomposition of the samples by the laser beam, 20% by weight samples in dry KBr were examined in rotating solid discs of conventional design. Laser

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excitation lines 488.0 and 514.5 nm were used with each compound.

The electronic absorption spectrum of the $K_2(Ti(O_2)(SO_4)_2)\cdot 5H_2O$ in 1 M H_2SO_4 was recorded using a Beckman-25 spectrometer.

Results and Discussion

The Raman spectra of $K_2(Ti(O_2)(SO_4)_2)\cdot 5H_2O$ and $K_2(Ti(O_2)(C_2O_4)_2)\cdot 3H_2O$ were recorded using the 488.0 and 514.5 nm excitation lines and resonance Raman enhancement was observed with both lines. Figure 1 shows the resonance Raman spectra using the 488.0 nm excitation. The resonance effects are associated with the electronic absorption band observed at 425 nm shown in Fig. 2. The Raman results are consistent with the triangulary bonded peroxide in the $Ti(O_2)$ unit of these complexes. This unit has local symmetry of C_{2v} and is expected to display three modes of vibrations distributed over the symmetry species $2A_1 + B_2$. These modes are designated as ν(O–O), (A_1); ν_s(Ti–O), (A_1); and ν_{as}(Ti–O), (B_2); all are Raman active and their assignments are given in Table I. The O–O stretching frequency occurs at 891 and 895 cm^{-1} for the sulphato and oxalato complexes, respectively. These values show that the ν(O–O) is not effected by changing the complexing agent coordinated to Ti(IV) and infering that mixing of ν(O–O) with $\nu(SO_4^{2-})$ or $\nu(C_2O_4^{2-})$ vibrations is slight or absent as would be expected from the triangular structure of $Ti(O_2)$ unit. It should be noted that the ν(O–O) values are higher than that of H_2O_2 at 877 cm^{-1} as a result of the expected π-donation from π^*–(O_2^{2-}) to the empty t_{2g} of Ti(IV) increasing the O–O bond strength and hence its frequency. The assignments of the Ti–O stretching frequencies agree with the literature values for related species as shown in Table II. The ν_s(Ti–O) occurs in both complexes around 610 cm^{-1}. The first and second overtones for such mode are also observed to be consistent with the resonance Raman condition. The ν_{as}(Ti–O) in the oxalato complex is assigned at 536 cm^{-1}. This agrees with the recent assignment of similar mode in $K(Ti(O_2)F_3)$ at 530 cm^{-1} [17]. The two Raman bands observed in the low region at 275 and 294 cm^{-1} in the spectra of the sulphato and oxalato complexes, respectively, are assigned to the bending motions of the type δ_s(OTiO′); O′ is the coordinated oxygen of SO_4^{2-} or $C_2O_4^{2-}$. These modes are expected to be resonance enhanced because of the involvement of the peroxo oxygens in such motions.

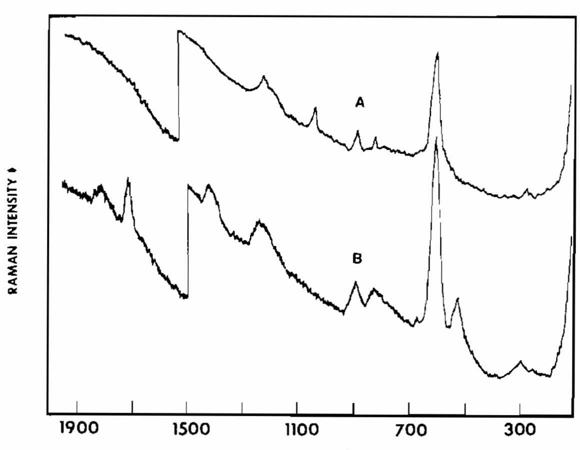


Fig. 1. Resonance Raman spectra of peroxotitanium(IV) complexes using 488.0 nm. (a) $K_2(Ti(O_2)(SO_4)_2)\cdot 5H_2O$; (b) $K_2(Ti(O_2)(C_2O_4)_2)\cdot 3H_2O$.

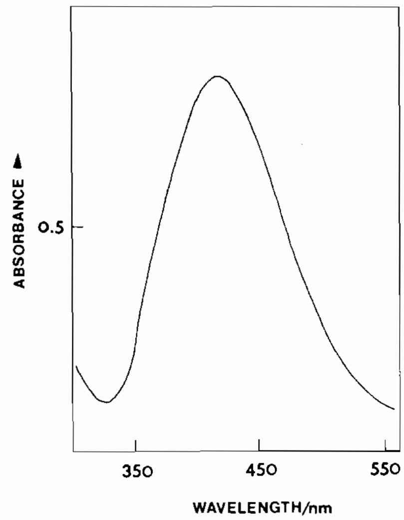


Fig. 2. Electronic absorption spectrum of $K_2(Ti(O_2)(SO_4)_2)\cdot 5H_2O$ in 1 M H_2SO_4.

TABLE I. Raman Bands[a] (cm^{-1}) for Peroxotitanate(IV) Complexes

$K_2(Ti(O_2)(SO_4)_2)\cdot 5H_2O$	$K_2(Ti(O_2)(C_2O_4)_2)\cdot 3H_2O$	Assignments
275w		δ_s(OTiO′)
	295w	δ_s(OTiO′)
	536mw	ν_{as}(Ti–O)
612s	611vs	ν_s(Ti–O)
891w	895mw	ν(O–O)
1043w		$\nu_s(SO_4^{2-})$[b]
1223w	1226w	$2\nu_s$(Ti–O)
	1432w	$\nu(C_2O_4^{2-})$[c]
	1730m	
	1826w	$3\nu_s$(Ti–O)

[a]s: strong, m: medium, w: weak, v: very. [b]Ref. 20. [c]Ref. 21.

TABLE II. Stretching Frequencies (cm^{-1}) for Peroxo Compounds

Compound	ν(O–O)	ν_s(M–O)	ν_{as}(M–O)	Reference
H_2O_2	877			22
$RhCl(O_2)(Pph_3)_2$(tert-BuNC)	892	576		23
NiO_2(tert-BuNC)$_2$	898	552		23
(Co(salen)(py))$_2O_2$	884	543		16
$K_6(Co(CN)_5)_2O_2$	804	602		15
$K(Ti(O_2)F_3)\cdot 3H_2O$	860, 900	610	530	17
$K_2(Ti(O_2)(SO_4)_2)\cdot 5H_2O$	891	612		Present work
$K_2(Ti(O_2)(C_2O_4)_2\cdot 3H_2O$	895	611	536	Present work

TABLE III. Observed and Calculated Frequencies (cm^{-1}) and Potential Energy Distributions for $Ti(O_2)$ Unit in $K_2(Ti(O_2)(C_2O_4)_2)\cdot 3H_2O$

Observed	Calculated	Potential energy distributions[a]		Assignments
		F_T	F_R	
895	901	72	23	76% ν(O–O) + 24% ν_s(Ti–O)
611	608	28	71	72% ν_s(Ti–O) + 28% ν(O–O)
536	537		100	ν_{as}(Ti–O)

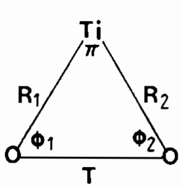
[a]Potential energy distributions total 100 including contributions from interaction constants, which are not shown.

As mentioned earlier the resonance effects in the Raman spectra of these peroxo complexes are associated with the absorption band at 425 nm. This band is assigned to the $O_2^{2-} \rightarrow Ti(IV)$, charge-transfer transition. This is evident from the enhancement of the Ti–O vibrational intensities compared with those of the SO_4^{2-} or $C_2O_4^{2-}$ in the corresponding peroxo complex. The intensity of the ν_s(Ti–O) measured relative to that of $\nu_s(SO_4^{2-})$ in the sulphato complex is increased from 2.9 to 7.1 upon changing the excitation wavelength from 514.5 to 488.0 nm towards the absorption maxima at 425 nm.

Force Constant Calculations

The calculations were carried out only for the $Ti(O_2)$ unit and based on the Wilson's GF matrix method [18]. A version of the Snyder–Schachtschneider programs was used in the computation process [19]. The bond lengths and angles of the $Ti(O_2)$ unit were taken from related species [7]. The O–O and Ti–O bond distances are 145 and 189 ppm, respectively; the OTiO angle measures 45.2°.

The six internal coordinates for $Ti(O_2)$ are defined as shown in Scheme 1.



Scheme 1.

The $Ti(O_2)$ unit belongs to the C_{2v} symmetry and should display only three vibrations, so three redundant coordinates exist. These are associated with the angle bends and were excluded in the calculations. The constructed symmetry coordinates are as follows:

A_1:$S_1 = T$ O–O stretching

$S_2 = (1/\sqrt{2})(R_1 + R_2)$ Ti–O stretching

B_2:$S_2 = (1/\sqrt{2})(R_1 - R_2)$ Ti–O stretching

The calculated values of the force constants F_T, F_R, F_{TR} and F_{RR} for the $Ti(O_2)$ are 320, 275, 11, and 21 N m^{-1}, respectively. The good fit between the observed and calculated frequencies as well as their potential energy distribution values support our assignments for $Ti(O_2)$ modes as given in Table III. The mixing between the ν(O–O) and ν_s(Ti–O)

TABLE IV. Force Constant Values N m^{-1}) for Peroxo Compounds

Compound	F_{O-O}	F_{M-O}	Reference
H_2O_2	384		22
NiO_2(tert-BuNC)$_2$	350	240	23
$RhO_2Cl(Pph_3)_2$(tert-BuNC)	330	320	23
$K_6(Co(CN)_5)_2O_2$	290	280	15
(Co(salen)(DMF))$_2O_2$	380	247	16
$K_2(Ti(O_2)(C_2O_4)_2)\cdot 3H_2O$	320	275	Present work

modes is normal, since both motions belong to the same A_1 symmetry block.

Finally, the values of force constants for the O_2^{2-} and Ti–O bonds are quite reasonable compared with those reported for other peroxo species as shown in Table IV.

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