RAMAN AND INFRARED STUDIES FOR $NbF_5O_2^{2-}$ ION

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The Raman and infrared spectra of $NbF_5O_2^-$ ion have been investigated. The observed bands are assigned on the basis of C_{2v} symmetry. The $\nu_{(0-0)}$, $\nu_{s(Nb-0)}$ and $\nu_{as\ (Nb-O)}$ stretching frequencies are observed at 955, 880 and 900 cm^{-1}, respectively.

INTRODUCTION

The peroxo compounds of transition elements are of special interest and growing importance in relation to the various types of metal ion-catalyzed reactions of hydrogen peroxide and molecular oxygen particularly in biological systems [1] such as the metal-centred proteins. Leavitt *et al.* [2, 3] have prepared the interesting peroxo species penta-fluoroperoxoniobate (V); $NbF_5O_2^{2-}$ ion, where niobium forms seven coordinates. Recently, Stomberg [4, 5] has reported the crystal structure of this ion in the form of $Na_2NbF_5O_2$ and $Na_3HF_2NbF_5O_2$. He has shown the symmetry of the $NbF_5O_2^{2-}$ ion assumes almost the C_{2V} point group where the peroxo group occupies two adjacent equatorial positions with O-O bond distance measuring 1.48 Å and the axial Nb-F bonds are shorter than these occupying the equatorial positions.

In a previous work these authors have applied successfully vibrational spectroscopic studies in investigating many short-lived [6] as well as stable [7] peroxo species of some metal complexes. Here these authors present the results collected from the Raman and infrared measurements of the peroxo ion $NbF_5O_2^{2-}$. The aim is to establish with the aid of group theoretical analysis the assignments of the different fundamental vibrational modes related to the metal-peroxo unit as well as those associated with different Nb-F bonds. This may enable us to understand the nature of bonding inherent in this compound.

EXPERIMENTAL

The solid peroxo compounds $Na_2NbF_5O_2$ and Na_3HF_2 NbF_5O_2 were prepared and characterized according to the

known methods [4, 5].

Spectroscopic measurements. Raman spectrum was measured with a Cary Model 82 spectrometer equipped with a coherent radiation Model 53 argon ion laser. Laser excitation lines 514.5 and 488.0 nm were selected to record the spectrum of the peroxo species. To prevent decomposition by the laser beam, the sample as a pressed disc (20% by weight in KBr), was spun at approximately 2000 rpm in a conventional rotating disc holder.

Infrared spectrum was recorded from potassium bromide disc (1% by weight) on a Pye Unicam SP 2000 infrared spectrometer.

RESULTS AND DISCUSSION

The Raman spectrum of $NbF_5O_2^{2-}$ ion recorded by applying the 514 nm laser excitation line is shown in Fig. 1. The corresponding infrared spectrum is indicated in Fig. 2. X-ray crystallographic studies [4, 5] on $NbF_5O_2^{2-}$ ion conclusively show that this species has the pentagonal — bipyramidal structure in which the peroxo group acts as a bidentate ligand and occupies two adjacent equatorial positions with (O-O) and (Nb-O) bond distances measuring 1.48 and 1.93 Å respectively. Three fluoride atoms occupy the remaining equatorial positions whereas the remaining two fluoride atoms occupy axial positions with shorter Nb-F bond distance measuring 1.92 Å. Accordingly, the $NbF_5O_2^{2-}$ ion possesses a C_{2v} symmetry and calculation predicts to display eighteen different modes of vibrations. These are resolved according to the vibrational representation:

$$\tau_{vib.} = 7A_1 + 2A_2 + 4B_1 + 5B_2$$

These eighteen non-degenerate modes are infrared and Raman active except for the A_2 modes which are only Raman active. Among these, $2A_1 + B_2$ modes are associa-

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Table 1. Various symmetry coordinates for $NbF_5O_2^{2-}$ ion

Symmetry species	Symmetry coordinate	Description
A_1	$S_1 = t$	$O - O$; stretch
	$S_2 = 1/\sqrt{2} \, (T_1 + T_2)$	$Nb - O$; stretch
	$S_3 = 1/\sqrt{2} \, (W_1 + W_2)$	$Nb - F'$; stretch
	$S_4 = R$	$Nb - F$; stretch
	$S_5 = 1/\sqrt{2} \, (r_1 + r_2)$	$Nb - F''$; stretch
	$S_6 = 1/\sqrt{2} \, (\alpha_1 + \alpha_2)$	F Nb F''; bend
	$S_7 = 1/\sqrt{2} \, (\delta_1 + \delta_2)$	F' Nb F''; bend
A_2	$S_8 = 1/\sqrt{4} \, (\oplus_1 - \circ_2 - \oplus_3 + \oplus_4)$	F Nb F'; bend
	$S_9 = 1/\sqrt{4} \, (\gamma_1 - \gamma_2 - \gamma_3 + \gamma_4)$	F' Nb O; bend
B_1	$S_{10} = 1/\sqrt{2} \, (W_1 - W_2)$	$Nb - F'$; stretch
	$S_{11} = 1/\sqrt{2} \, (\delta_1 - \delta_2)$	F' Nb F''; bend
	$S_{12} = 1/\sqrt{4} \, (\gamma_1 + \gamma_2 - \gamma_3 - \gamma_4)$	F' Nb O bend
	$S_{13} = 1/\sqrt{4} \, (\phi_1 + \phi_2 + \phi_3 - \phi_4)$	F Nb F'; bend
B_2	$S_{14} = 1/\sqrt{2} \, (T_1 - T_2)$	$Nb - O$ stretch
	$S_{15} = 1/\sqrt{2} \, (r_1 - r_2)$	$Nb - F$ stretch
	$S_{16} = 1/\sqrt{2} \, (\alpha_1 - \alpha_2)$	F Nb F'' bend
	$S_{17} = 1/\sqrt{2} \, (B_1 - B_2)$	F Nb O bend
	$S_{18} = 1/\sqrt{2} \, (C_1 - C_2)$	Expressed in S_{14}

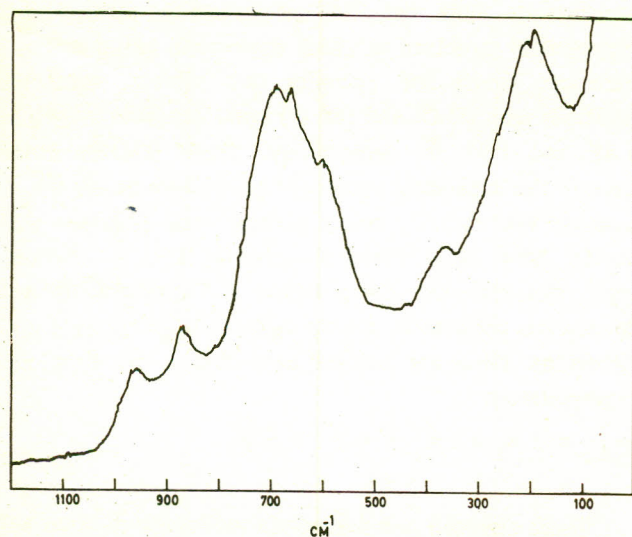ted to the NbO_2 unit (local symmetry of C_{2v} as of the entire molecule). These are designated as $\nu_{(0-0)}$; (A_1) and Nb-O stretching vibrations $(A_1 + B_2)$. The remaining modes, five out of them $3 A_1 + B_1 + B_2$, belong to different Nb-F stretching vibrations while the angle bends are associated with $2 A_1 + 2 A_2 + 3 B_1 + 3 B_2$ vibrational modes.

In order to perform accurate assignments, the molecular vibrational motions of polyatomic molecules, however, may be best described in terms of symmetry coordinates [8]. These were constructed for the $NbF_5O_2^{2-}$ ion exhibiting the C_{2v} symmetry using the internal coordinates defined in Fig. 3 and tabulated in Table 1.

Band assignments. The observed infrared and Raman bands are assigned as indicated in Table 2. As mentioned before, the NbO_2 unit in $NbF_5O_2^{2-}$ ion is expected to diplay three modes of vibration. Thus the Raman band at 955 cm^{-1} is assigned to the O-O stretching vibration [5]. while the symmetric and anti-symmetric Nb-O stretching vibrations S_2 and S_{14} are assigned to the Raman band at 880 cm^{-1} and the infrared band at 900 cm^{-1} respectively.

Fig. 1. Raman spectrum of $NbF_5O_2^{2-}$

Table 2. Infrared and Raman bands for $NbF_5O_2^{2-}$ ion in cm^{-1}

Infrared	Raman	Assignments	
	955 m	A_1 :	$v_1 ; O - O$ str.
	880 m		$v_2 ; Nb - O$ str.
	696 s		$v_3 ; Nb - F''$ str.
650 W	660 s		$v_4 ; Nb - F''$ str.
	608 m		$v_5 ; Nb - F''$ str.
	215 s		$v_6 ; F Nb F''$ bend.
	195 s		$V_7 ; F Nb F''$ bend.
730 s	728 sh	B_1 :	$v_{10} ; Nb - F'$ str.
497 m			$v_{12} ; F' Nb O$ bend
900 w		B_2	$v_{14} : Nb - O$ str.
730 s			$v_{15} ; Nb - F$ str.
481 m			$v_{17} ; F Nb O$ bend
1195 w			$v_{10} + v_{17}$
1450 w			$2 v_{10}$

* s = strong, m = medium, w = weak, sh = shoulder.
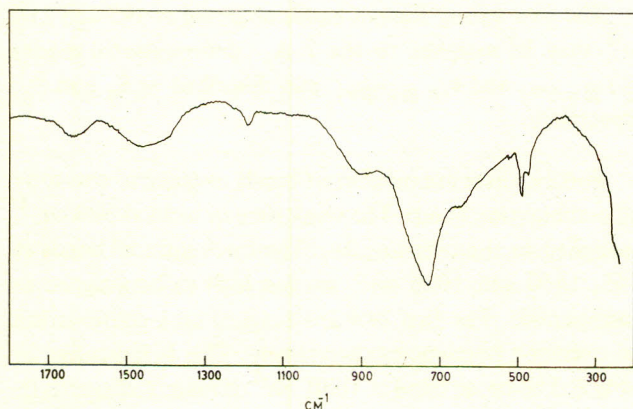
Fig. 2. Infrared spectrum of $NbF_5O_2^{2-}$

Although the assignments of these Nb-O modes are based on their intensities and they also are in agreement with the reported [9, 10] wave numbers for the other niobium (V) — oxygen species, however, the value of wave number for the peroxo as well as the Nb-O stretching vibrations in $NbF_5O_2^{2-}$ ion are somewhat higher than those reported for other metal-peroxo species as illustrated in Table 3. This may be understood from the fact that when the proxo group coordinates to Nb (V) central atom the

process is expected to involve both σ and π — donation from the ligand to the metal ion. This is probably expected to strengthen the Nb-O bonds and hence reflects the higher values of their stretching wave number. Such donation is very likely to take place because of the very high positive charge surrounding the niobium atom and also the deprivation of its d-orbital from its electons. However, the π — donation of electrons from the peroxo group is expected to come from its π^* — molecular orbital (Fig. 4). This would increase the O-O bond order and hence its stretching wave number compared with H_2O_2 and other peroxo compounds.

The assignment of the various modes associated with the metal fluoride bonds in $NbF_5O_2^{2-}$ ion may be achieved by considering the assignments reported for some related niobium (V)—halogen compounds such as NbX_5. Com-
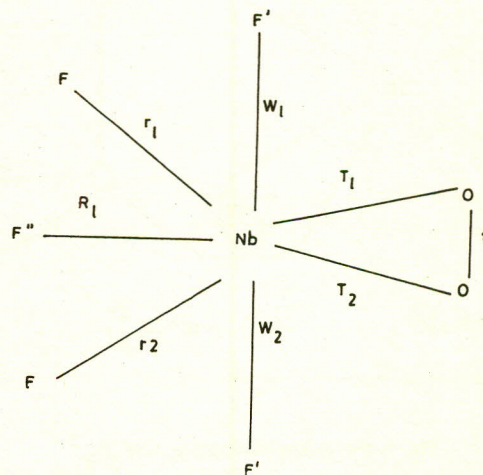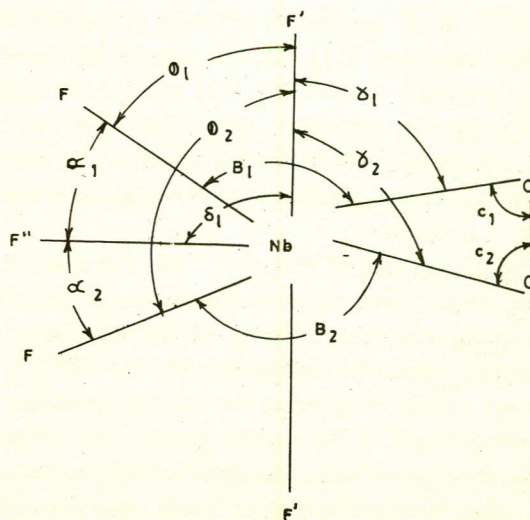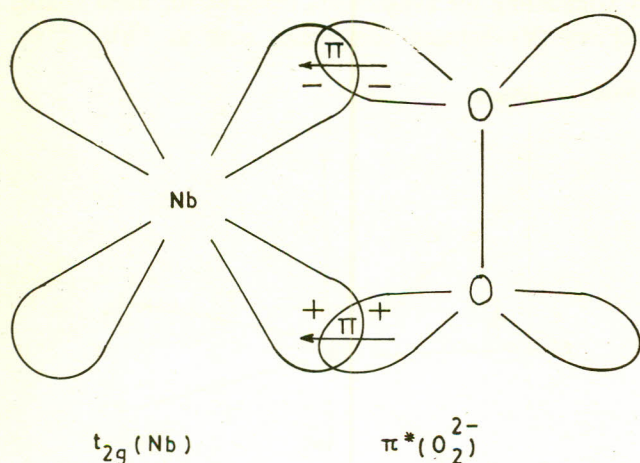

Fig. 3. Definition of the internal coordinates in $NbF_5O_2^{2-}$

Table 3. Vibrational wave numbers (cm^{-1} of the peroxo and peroxo-metal links in different compounds

Compound	$\nu_{(O-O)}$	$\nu_{(M-O)}$	Ref.
H_2O_2	880	–	15
$((CN)_5 CoO_2 Co(CN)_5)^{6-}$	880	610	7
$((DMSO)(Salen)CoO_2 Co(Salen)(DMSO)$	876	532	7
$CrO_5 \cdot H_2O$	1012	522,496	6
$(Fe(EDTA)(O_2))^{3-}$	824	–	6
$(VO(O)(HO)(bipicoline))^-$	839	610-570	16
$(NbF_5 O_2)^{2-}$	955	900,880	This work

$t_{2g}(Nb)$ $\pi^*(O_2^{2-})$

Fig. 4. π-bonding involved in $NbF_5 O_2^{2-}$

pounds of the latter are known to belong to two different geometrical structures [11] viz, the trigonal-bipyramidal with D_{3h} symmetry as in $NbCl_5$ [12] and the tetragonal-pyramidal with C_{4v} symmetry, as in NbF_5 [13]. In the first, the equatorial Nb-X bonds are shown to be shorter than those in the axial positions, but the situation is found to be reverse in the latter.

In the present case of $NbF_5 O_2^{2-}$ ion, the axial Nb-F bonds are shorter than those in the equatorial positions which is similar to the case of NbF_5. On the other hand, we may further confirm the assignments for the $NbF_5 O_2^{2-}$ ion through closely considering the relative intensities of the observed bands of the present species and compare them with those reported assignments for NbF_5 compound [14], e.g. the three strong Raman bands observed in the spectrum of $NbF_5 O_2^{2-}$ ion at 696, 660 and 608 cm^{-1} should be associated with the different symmetric Nb-F

vibrations. These include $\nu_{(Nb-F)}$", $\nu_{(Nb-F)}$ and $\nu_{(Nb-F)}$" and described as S_3, S_5 and S_4 respectively. The remaining two Nb-F vibrations S_{10} and S_{15} are associated with the antisymmetric motions and are assigned to the broad strong infrared band centred at 730 cm^{-1}. There are two bands observed only in the infrared spectrum with medium intensities at 481 and 497 cm^{-1}. These bands are tentatively assigned to the two deformation modes; $\nu_{(F',Nb\,0)}$ and $\nu_{(FNb\,O)}$, described as S_{12} and S_{17} respectively. Such vibrational motions are expected to be weak in the Raman spectrum.

The two strong Raman bands observed at 195 and 215 cm^{-1} may be assigned to the 2 A_1 deformational modes, $\nu_{(F'\,Nb\,F'')}$ and $\nu_{(F\,Nb\,F'')}$, and described as S_7 and S_6, respectively.

Finally, there are number of bands assigned to overtone and combination bands. The weak Raman band at 380 cm^{-1} is assigned to the overtone $2\nu_7$. The three infrared bands at 1195, 1450 and 1630 cm^{-1} are too high to be assigned as fundamentals. The first two are assigned to a combination and overtone frequencies respectively. This is illustrated in Table 2. The broad band at 1630 cm^{-1} is mainly characterized to the free water.

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