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IR and Laser Raman Studies on Peroxo Fluoro Species of Zirconium

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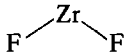
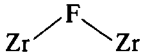
Infrared (IR) and laser Raman spectra of new peroxo fluoro species of zirconium, $M_3[Zr_2(O_2)_2F_7](0.6–2)H_2O$, where M is K, Rb Cs and NH_4, have been studied. The characteristic band due to ν(O–O) vibration is observed around 840–850 cm^{-1} both in IR and Raman spectra, showing the presence of triangularly linked bidentate peroxo group in them. The IR spectra of the species exhibit broad absorption envelopes around 375–475 and 240–350 cm^{-1} attributable to Zr–F stretching and



bending vibrations. The strong Raman band observed around 150–160 cm^{-1} is assigned to the symmetric vibration involving bridged fluorine in a



type linkage. The water associated with the species is lattice held.

Introduction

Very little is known in the field of peroxo fluoro species of zirconium [1]. Work is in progress in this laboratory on peroxo fluoro species of transition elements. The present paper deals with the IR and laser Raman spectral studies of new peroxo fluoro species of zirconium synthesized by us.

Experimental

Materials and Methods

Zirconium oxide chloride octahydrate, $ZrOCl_2 \cdot 8H_2O$ (A.R. grade, procured from Bhabha Atomic Research Centre–BARC, Bombay, India), hydrogen peroxide (30%), potassium fluoride (anhydrous), ammonium fluoride, rubidium carbonate, caesium carbonate, hydrofluoric acid (40%), and methanol of B.D.H. quality were employed for the preparative work.

A weighed quantity (4.5 g) of zirconium oxide chloride octahydrate was dissolved in 100 ml of 1:1 mixture of water and methanol. Hydrogen peroxide (30%) was added in slight excess to the above solution. This was followed by the slow addition of a solution of potassium fluoride (in water–methanol mixture) maintaining the mol ratio of zirconium to fluoride as 1:5 to 1:7 in the mixture. A white solid separated immediately. It was allowed to remain in the mother liquor for an hour, separated by filtration, washed well and dried.

The dried solids were analysed for their constituents by standard methods [2]. Ion sensitive electrode (Orion fluoride sensitive electrode, model 94 - 09A) method was used for estimating fluoride [3]. The water content was computed by difference. A representative sample analysed as:

Constituents	Zr		O_A		F^-		K^+		H_2O (by diff.)
% values	34.51		6.06		25.47		21.06		6.84
Molar ratio	1	:	1.00	:	3.54	:	1.42	:	1.00

The water content was found to be varying in the range of 0.3–1 mol per zirconium atom in different preparations. The species is formulated as $K_3Zr_2(O_2)_2F_7(0.6–2)H_2O$.

The peroxo fluoro zirconate(IV) species were also prepared with rubidium, caesium and ammonium cations. The resulting solids were test checked for some of their constituents, *e.g.*, the rubidium peroxo fluoro zirconate(IV) analysed as:

	Zr		O_A		Rb^+
% value	29.96		5.54		39.98
Molar ratio	1	:	1.05	:	1.42

The species are found to possess the same molar composition, and are formulated as: $M_3Zr_2(O_2)_2F_7(0.6–2)H_2O$, where M is K, Rb, Cs, NH_4.

Physico-chemical Studies

The IR spectra of the solids were recorded both in nujol mull and in KBr pellet on Grubb Parsons IR spectrophotometers; SP/MKIII (4000–400 cm^{-1}) and DM4 (500–200 cm^{-1}). The Raman spectra, recorded

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on a Cary 82 Raman spectrophotometer using a He–Ne laser source (6328Å) for excitation, were obtained from an outside laboratory.

Some General Properties of the Species

The present compounds are white crystalline solids soluble in mineral acids, but insoluble in routine organic solvents. They contain true peroxo groups [4] which are found to be relatively stable. There is practically no loss of active oxygen (O_A) on storage. Water associated with the species is lattice held, as most of it is lost at about 120 °C. They do not contain hydroxyl groups [5].

Results and Discussion

The salient features of the IR spectra are presented in Fig. 1 and those of Raman spectra in Fig. 2. The observed IR and Raman bands are listed in Table I. The tentative assignments are based on the available literature data.

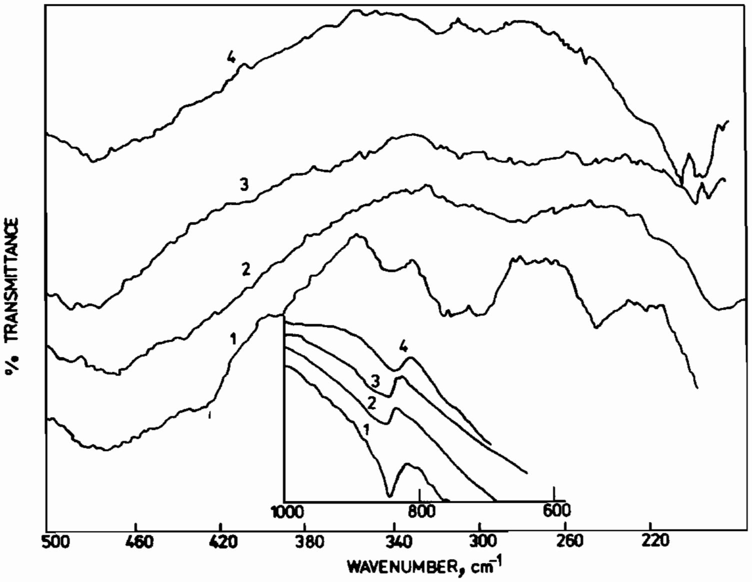


Figure 1. Salient features of the IR spectra of peroxofluoro zirconates(IV). (1) Potassium, (2) rubidium, (3) caesium and (4) ammonium species.

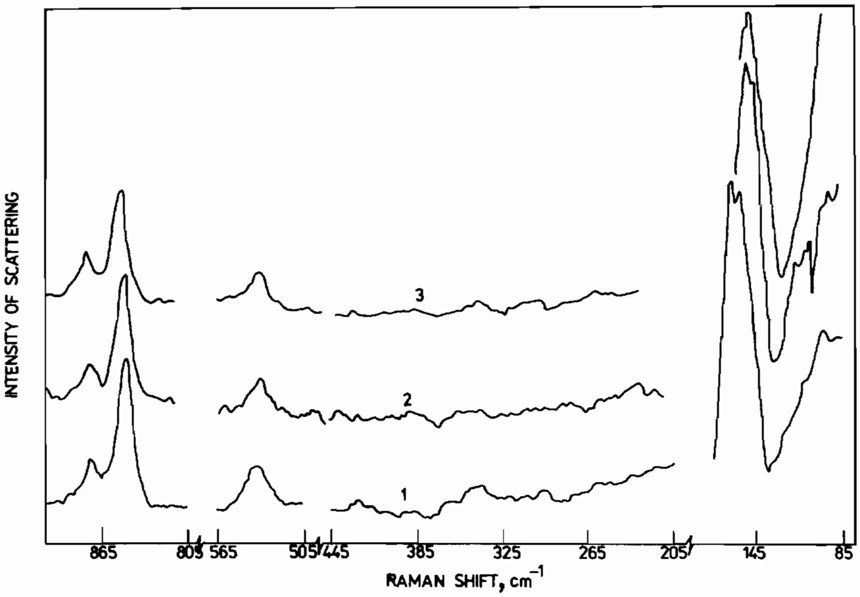
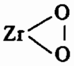
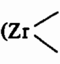
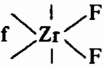
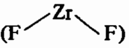
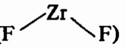
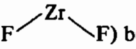
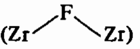


Figure 2. Salient features of the Raman spectra of peroxofluoro zirconates(IV). (1) Potassium, (2) rubidium, (3) caesium.

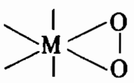
TABLE I. IR and Raman Data of Peroxo Fluoro Zirconate(IV) Species.[a]

Potassium		Rubidium		Caesium		Ammonium	Assignments
IR (cm^{-1})	Raman Shift (cm^{-1})	IR (cm^{-1})	Raman Shift (cm^{-1})	IR (cm^{-1})	Raman Shift (cm^{-1})	IR (cm^{-1})	
3420 vs&b	–	3480 vs&b	–	3500 vs&b	–	3480 s	ν_{as}(O–H) of H_2O
–	–	–	–	–	–	3200 s&b	$\nu(NH_4^+)$
1640 s&b	–	1650 s&b	–	1650 s&b	–	1630 s&b	δ(H–O–H) of H_2O
–	–	–	–	–	–	1400 s&b	$\nu_4(NH_4^+)$
–	–	1080 w	–	1090 w	–	–	–
–	–	1020 w	–	1020 w	–	–	–
–	876(2)	–	874(2)	–	875(2)	–	–
840 m	850(5)	850 m	850(5)	850 m	850(5)	850 m	ν_1(O–O) of 
590 s	–	590 s	–	600 s	–	600 s	ν() asymmetric stretch together with Zr–F stretch
–	536(2)	–	536(2)	–	538(2)	–	symmetric metal peroxide stretch
475 vs&b	505(1)	470 vs&b	505(1)	480 vs&b	500(1)	475 vs&b	ν_{as}(Zr–F) stretch of 
430 sh	425(1)	435 sh	428(1)	430 sh	440(1)	430 sh	
395 w	390(1)	375 sh	385(1)	380 sh	390(1)	400 sh	ν(Zr–F) stretch
340 m&b	340(1)	330 w	340(1)	350 w&b	340(1)	345 w	ν_{as}() stretch
320 s	296(1)	310 s	298(1)	305 m	–	310 s	ν_s() stretch
300 s		280 s		275 m		285 s	
245 s	–	245 m	–	240 m&b		240 m	δ() bending
–	160(10)	–	153(10)	–	148(10)	–	ν_s() stretch

[a] vs = very strong; s = strong; b = broad; m = medium; ν = stretching; δ = bending; as = asymmetric; s = symmetric; sh = shoulder. Relative intensities of Raman lines given in parentheses.

Peroxo Group

Vibrational spectra have been successfully employed in the characterization of peroxo group linkages in transition metal peroxo complexes [6–10]. A triangularly linked bidentate peroxo group,

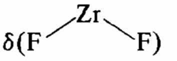


(C_{2v}), gives rise to three vibrations which are both IR and Raman active [6–8]. The characteristic stretching vibration, ν_1(O–O) is observed around 850–880 cm^{-1} whereas ν_2 and ν_3 which involve metal oxygen stretches appear weak in the region 500–600 cm^{-1}. Further, it is difficult to assign ν_2 and ν_3 in peroxo fluoro species because of the presence of metal fluorine stretching modes in the same region, and it has also been observed in oxofluoro complexes that metal fluorine stretches are exceedingly weak for the solid state Raman spectra [11]. It is thus seen that ν(O–O) alone is of diagnostic help in deciding the nature of the 'O–O' group in peroxo species. In the case of a triangularly linked bidentate peroxo group, ν(O–O) would be observed both in IR and Raman spectra whereas a bridging type peroxo group (C_2) shows no IR absorption, but gives a strong Raman band [6, 8, 10].

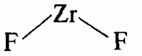
It is seen from the spectral data of the present compounds that the characteristic ν(O–O) band is observed around 840–850 cm^{-1} both in IR and Raman spectra. This indicates the presence of triangularly linked bidentate peroxo groups.

Metal Fluorine Vibrations

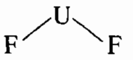
It is seen from the literature that the metal fluorine stretching and bending vibrations appear, moderately strong in intensity [12, 13] below 600 cm^{-1}. At these low frequencies, there would be extensive coupling between various modes of vibrations and hence it is difficult to consider them as pure vibrations [13]. Despite this, very valuable and useful correlations have been worked out for terminally linked metal fluorine vibrations [13]. Smith and coworkers [14] have noticed that terminally linked zirconium fluorine stretching vibrations appear in the region 380–550 cm^{-1} and the bending vibrations



in the region 200–350 cm^{-1} in fluoro complexes of zirconium. Goldstein *et al.* [15] have also assigned the broad band around 465 cm^{-1} to terminally linked metal fluorine stretching vibrations and the one observed around 250 cm^{-1} to

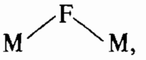


bending vibration in the spectra of zirconium tetrafluoride. Dao *et al.* have observed [16–18] that the terminally linked U–F stretching frequencies fall in the region 318–470 cm^{-1} and the

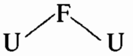


bending vibrations between 200–230 cm^{-1}.

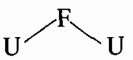
The metal fluorine vibrations involving the fluorine bridged system,



which fall still at lower frequencies are more difficult to assign [13]. But the very recent work of Dao *et al.* [16] has characterized for the first time the bridged metal fluorine vibrations in $[U(O_2)_2F_9]^{5-}$ species. The bridged fluorine system,

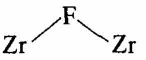


(C_{2v}), should show three vibrations which are both IR and Raman [13] active. The above authors have assigned the IR frequencies at 129 and 119 cm^{-1} to the stretching vibrations of the bridged



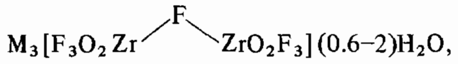
system [13]. The Raman band due to symmetric vibration of the bridged fluorine is observed around 156 cm^{-1}. However, the bands observed below 100 cm^{-1} may also be affected due to lattice modes.

The present species show in IR broad absorption envelopes around 375–475 and 240–350 cm^{-1}, attributable to the stretching and bending vibrations respectively involving the terminally linked fluorines to zirconium. The strong Raman band around 150–160 cm^{-1} (Fig. 2) is attributed to the symmetric vibration of



type linkage, based on the work of Dao *et al.* [13].

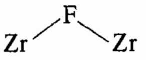
It is thus seen that the present species contain terminally linked as well as bridging type fluorines. They could be formulated as



$M_3[F_3O_2Zr\overset{F}{\frown}ZrO_2F_3](0.6\text{–}2)H_2O$,

where M is K, Rb, Cs or NH_4.

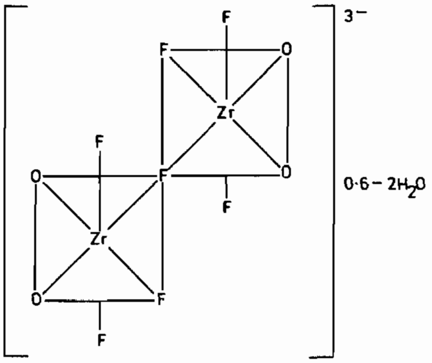
There is ample literature evidence showing the bridging tendency of fluorine in several simple fluorides and fluorometallates of transition elements [19–22]. Even zirconium tetrafluoride is a polymer with



bridges [21].

Summary and Conclusions

The present species contain true peroxo groups which are triangularly linked bidentate in nature. They also contain terminally linked as well as bridging type fluorines. The water molecules are lattice held. The species could best be represented as below:



The negative charge is neutralized by the cations. In the above representation, zirconium exhibits coordination number 6 and the two octahedra are sharing a fluorine on the edge. There is evidence in the literature for such structural representations incorporating the sharing of a common edge by two octahedra [22]. The above structure explains all the observed experimental findings.

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