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Infrared and Raman Studies of the $[VO(O_2)_2F]^{2-}$ Ion

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The IR and Raman spectra of Cs_2 $[VO(O_2)_2F]$ are recorded. The spectra are interpreted on the basis of C_s symmetry of the $[VO(O_2)_2F]^{2-}$ ion. The ν(V=O), ν_s(O–O), and ν_{as}(O–O) are assigned at 950, 890, and 875 cm^{-1}, respectively. The calculated values of the force constants $f_{V=O}$, f_{O-O}, f_{V-O}, $f_{V-O'}$, and f_{V-F} are 670, 298, 262, 273, and 248 N m^{-1}, respectively. The band assignments and the force constant values are discussed in view of the bonding and structure of the $[VO(O_2)_2F]^{2-}$ ion.

In recent years the study of the peroxovanadium chemistry has attracted considerable interest and growing importance,[1–7] since the compounds have much relation to the various types of metal-centered biological systems such as the oxygen carriers as well as the peroxidase and catalase enzymes.[8–10] Most of these studies on peroxovanadium compounds are concerned mainly with their syntheses and structures and in some cases along with vibrational qualitative assignments of the bands, relatively few detailed vibrational works have been elucidated.

Although the reaction between vanadium(V) and H_2O_2 is complicated and pH dependent, many peroxovanadium(V) species have recently been prepared in pure forms. In 1980 Jere and Kaushik[4] reported the isolation of the first fluoro-peroxo species of vanadium(V), $K_2[VO(O_2)_2F]$. A general method for the preparation of different alkali fluorooxodiperoxovanadates(V), $A_2[VO(O_2)_2F]$, was later reported by Chaudhuri and Ghosh.[11].

In previous communications[12–14] detailed vibrational studies have been successfully carried out for many peroxometal species. In this work we report the quantitative vibrational assignments for an oxodiperoxovanadium species based on the IR and Raman spectra of $Cs_2[VO(O_2)_2F]$ and with the aid of normal coordinate analysis. The force constant values for the different bonds and angle bends are calculated. This enable an assessment of the type of bonding and structure inherent in this type of oxodiperoxo compounds.

Experimental

The soild oxodiperoxo compound $Cs_2[VO(O_2)_2F]$ was prepared according to the published method.[11] The chemical composition and IR spectrum agreed with the literature data.[11]

Spectroscopic Measurements. The Raman spectrum of $Cs_2[VO(O_2)_2F]$ was measured using a Carry Model 82 spectrometer and a Coherent Radiation Innova 12 argon ion laser with excitation lines 488.0 and 514.5 nm. To prevent photochemical and thermal 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. The IR spectrum of the compound was recorded for the sample as a KBr disc using a Pye Unicam SP 2000 spectrometer.

Results and Discussion

The IR spectrum of $Cs_2[VO(O_2)_2F]$ is shown in Fig. 1, and its Raman spectrum recorded using the

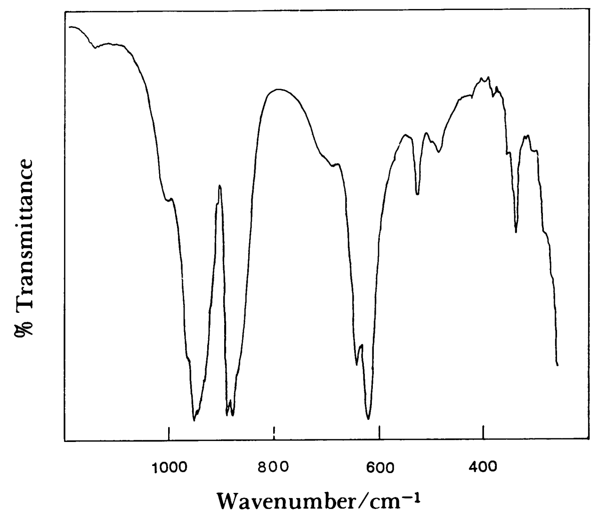

Fig. 1. Infrared spectrum of $Cs_2[VO(O_2)_2F]$.

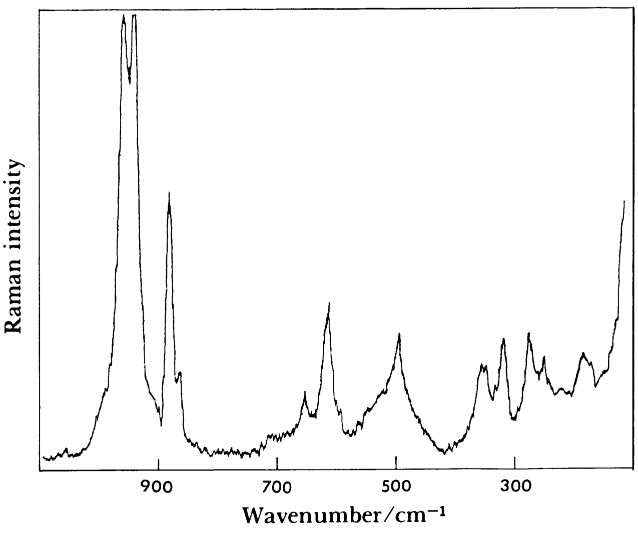

Fig. 2. Raman spectrum of $Cs_2[VO(O_2)_2F]$.

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488.0 nm excitation line is shown in Fig. 2. Before discussing the assignments of these spectra, the geometry of the ion $[VO(O_2)_2F]^{2-}$ must be considered. Here, the vanadium is six coordinate and from the IR and Raman band activities of the O_2^{2-} groups (Table 2), it is clear that each of the peroxy groups acts as a bidentate ligand forming a triangular shape with a vanadium. In this case two structures for the $[VO(O_2)_2F]^{2-}$ are possible. In the first structure both the vanadyl oxygen and the fluoride occupy the two axial positions while the two peroxo groups occupy the four equatorial positions. In this case the ion belongs to the C_{2v} symmetry. The other possible structure contains the two peroxo groups and the fluoride coordinated to vanadium in one plane with the vanadyl oxygen perpendicular to such a plane (Fig. 3). In this case the $[VO(O_2)_2F]^{2-}$ ion belongs to the C_s symmetry. This C_s structure may be the most probable one based on the fact that the reported crystal structure[7] of the related species $NH_4[VO(O_2)_2(NH_3)]$ indicates that the vanadium(V) is bonded to five oxygens and one nitrogen atoms: the coordination structure can best be described as a pentagonal pyramid. The four oxygens of the two peroxo groups, which are related by the mirror plane, and the ammonia nitrogen form the base of a distorted pyramid, and the vanadyl oxygen occupies the apical position. The V–O, V=O, V–N, and O–O bond lengths are 1.883, 1.606, 2.110, and 1.472 Å, respectively. Moreover, the predicted C_s structure for $[VO(O_2)_2F]^{2-}$ ion is also related to those of $[CrO(O_2)_2py]$ and $[CrO(O_2)_2(H_2O)]$.[15,16] Accordingly, the modes of vibrations of $[VO(O_2)_2F]^{2-}$ ion with the pentagonal pyramidal structure in the C_s symmetry, are distributed amongst the vibrational representation: $9A'+6A''$. This gives 15 non-degenerate modes, all are being both infrared and Raman active. From the fifteen fundamentals two modes of the type A′ belong to V=O and V–F bond stretches. The diperoxovanadium unit, $V(O_2)_2$ which possesses a local symmetry of C_{2v}, has six modes of bond vibrations, $3A'+3A''$. These are designated as ν(O–O); A′, ν(O–O); A″, ν(V–O); 2A′, and ν(V–O); 2A″. The remaining seven modes, 4A′ and 3A″ are associated with the different angle bends.

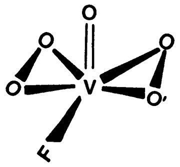

Fig. 3. Geometry of the $[VO(O_2)_2F]$ ion.

Table 1. Force Constants for $[VO(O_2)_2F]^{2-}$ Ion

Symbol	Description	Value[a)]
f_Q	V=O	670
f_R	O–O	298
f_r	V–O	262
$f_{r'}$	V–O′	273
f_w	V–F	248
f_β	O=V–O	87
$f_{\beta'}$	O=V–O′	96
f_α	F–V–O′	93
f_ϕ	O=V–F	105
f_π	O–V–O	116
f_{rr}		13
f_{Rr}		11
$f_{r'r'}$		14
$f_{r'w}$		8
$f_{\beta\beta}$		9
$f_{\alpha\alpha}$		12
$f_{\beta\beta'}$		9
$f_{\beta'\beta'}$		10

a) Stetching constants in $N\,m^{-1}$, bending constants in $N\,m^{-1}\,Rad.^2$.

Band Assignments. The observed IR and Raman bands are quantitatively assigned as indicated in Table 2 based on the C_s symmetry and the band intensities and with the aid of a complete normal coordinate analysis. This analysis was carried out on the basis of Wilson's GF matrix method;[17] a general quadratic potential energy function was applied utilizing no nonbonded interactions. A version of the Schachschneider programs[18] was used in the computation process. The details of the calculations are similar to those described previously.[19,20] However, in the calculation we faced with the problem that the number of the force constants exceeds the number of the observed frequencies which made it difficult to determine a complete set of force constants for $[VO(O_2)_2F]^{2-}$ ion. Therefore, the force field was simplified to include only the most effective interaction constants beside the diagonal constants. The initial set of force constants involved only the diagonal constants was first introduced and these were chosen in comparison with the known values of related peroxo compounds.[12] These values were systematically refined to obtain the best fit between the observed and calculated frequencies. The next step was to determine the effective off-diagonal constants by studying the effect of change in the value of each of the interaction force constants on values of the calculated frequencies as well as the physically acceptable potential energy distributions as shown in Table 2. This type of simplifying the force field has been successfully used by many workers.[21,22] The final set of the force constant values and their description are given in Table 1. The ν(V=O); A′ is assigned to the IR band at $952\,cm^{-1}$ and to the Raman doublet at 955 and $942\,cm^{-1}$. This doublet structure may infer the existence of solid-solid interaction between the vanadyl oxygen of one ion and the vanadium of another.[7] This assignments for ν(V=O) agree well with the known values reported for other vanadyl species.[4,11,23]

Table 2. Observed and Calculated Frequencies (cm^{-1}), Potential Energy Distributions and Quantitative Vibrational Assignments for $[VO(O_2)_2F]^{2-}$ Ion

Frequency			Potential energy distribution										Assignment
Obsd		Calcd											
IR	Raman		f_Q	f_R	f_r	$f_{r'}$	f_w	f_β	$f_{\beta'}$	f_α	f_ϕ	f_π	
952s	955vs 942vs	953	100	0	0	0	0	0	0	0	0	0	A′ : ν(V=O)
890s	882s	883	0	81	6	8	0	0	0	1	0	4	81% ν(O–O), 6% ν(V–O), 8% ν(V–O′).
653m	650m	641	0	0	21	32	34	1	1	2	3	5	21% ν(V–O), 32% ν(V–O′), 34% ν(V–F).
—	495m	497	0	3	54	2	37	0	0	0	0	4	54% ν(V–O), 37% ν(V–F).
485m	—	489	0	5	13	52	24	0	0	2	0	4	13% ν(V–O), 52% ν(V–O′), 24% ν(V–F).
340ms	323m	342	1	0	0	1	6	4	21	3	59	5	21% δ(O=V–O′), 59% δ(O=V–F).
—	280m	274	0	3	0	2	4	2	4	26	5	55	26% δ(F–V–O′), 55% δ(O–V–O).
—	248w	241	1	0	0	0	0	76	15	2	3	2	76% δ(O=V–O), 15% δ(O=V–O′).
—	180	175	0	0	0	0	0	20	51	0	29	0	20% δ(O=V–O), 51% δ(O=V–O′), 29% δ(O=V–F).
875s	872w	879	0	62	16	19	0	0	0	3	0	0	A″: 62% ν(O–O), 16% ν(V–O), 19% ν(V–O′).
618s	622s	629	0	34	27	32	0	3	4	0	0	0	34% ν(O–O), 27% ν(V–O), 32% ν(V–O′).
526m	522w	520	0	0	54	46	0	0	0	0	0	0	54% ν(V–O), 46% ν(V–O′).
365w	363m	366	0	0	3	2	0	43	50	2	0	0	43% δ(O=V–O), 50% δ(O=V–O′).
250w	—	257	0	2	0	0	0	1	1	96	0	0	96% δ(F–V–O′).
—	—	169	0	0	0	0	0	55	45	0	0	0	55% δ(O=V–O), 45% δ(O=V–O′).

Normalized to total 100 for the diagonal force constant distributions. Vibrations with more than 5% contribution are only listed.

The O–O bond vibrations are assigned to the bands around 890 and 875 cm^{-1} due to the ν_s(O–O); A′ and ν_{as}(O–O); A″, respectively. The observation of these two modes in both the IR and Raman spectra supports the triangular structure of $V(O_2)$ units (Fig. 3). Under such a structure, ν_s(O–O) and ν_{as}(O–O) belong to A′ and A″ symmetries, respectively, and both should be IR and Raman active. These values of ν(O–O) occur at much higher frequencies compared with that of the simple peroxide salts. The ν(O–O) in Li_2O_2 occurs at 802 cm^{-1}.[24] The higher value of ν(O–O) in our ion $[VO(O_2)_2F]^{2-}$ may be due to the π-donation from the filled π* orbitals of the O_2^{2-} to the empty d-orbitals of vanadium(V); the peroxide bond order, and hence its frequency should be increased. However, we believe that such π-donation from the peroxide should be much stronger than that reflected as an increase in the ν(O–O) value. This conclusion is based on the P.E.D. values (Table 2) which demonstrate a relatively strong coupling between the ν(O–O) and the ν(V–O) vibrations; the coupling is expected to lower the ν(O–O) value. The assignments of the other ν(V–O) and ν(V–F) frequencies are rather difficult. This arises from the very strong coupling between these motions as indicated from the P.E.D. values for each band as shown in Table 2. This type of strong mixing is expected from the closed system of $V(O_2)_2$ beside the existence of all of these atoms in one plane. However, the ν_s(V–O) and ν_{as}(V–O) could be assigned to the infrared and Raman bands observed around 650 and 620 cm^{-1}, respectively. The corresponding frequencies for the V–O′ bond vibrations are 485 and 526 cm^{-1}. The ν(V–F) is assigned to the Raman band at 495 cm^{-1}.

The calculated force constant values for the O–O and V=O bonds are 298 and 670 N m^{-1} respectively, while the average value of the V–O bonds is 268 N m^{-1}.

The higher value of the $f_{V=O}$ agrees with the double bond character of the vanadyl bond. Using the bond stretching force constant as an approximate measure of the relative equilibrium bond strength, it appears that the vanadyl link is ≈2.5 times stronger than the vanadium-peroxo link.

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