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VIBRATIONAL ASSIGNMENT AND NORMAL COORDINATE ANALYSIS OF $[MOF_5]^{2-}$ (M = Nb, Ta) IN THE MODIFIED UREY-BRADLEY FORCE FIELD

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SUMMARY

The force constants of $[NbOF_5]^{2-}$ and $[TaOF_5]^{2-}$ have been calculated using Wilson's FG matrix method. Previously reported vibrational frequency data have been used. A modified Urey-Bradley force field has been employed for the calculations.

With the initial set of values transferred from related force fields, the results demonstrate the localised nature of the vibrations and the easy transferability of Urey-Bradley force constants The assignments are generally consistent with previous empirical assignments.

INTRODUCTION

Owing to their applications as solid state materials (1), the spectroscopic and structural studies on oxofluoro metallates and oxofluorides have received impetus in recent years. Though the vibrational spectra of several oxofluoro complexes have been reported (2-9), complete normal coordinate analyses have been carried out for very few systems (4,5). In this context, it was

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of interest to perform the normal coordinate calculations for Rb_2NbOF_5 and Cs_2TaOF_5 and compare the results with those of related systems to note the consistency in the force constants and assignments obtained. A modified Urey-Bradley force field has been employed. The vibrational spectra have been reported by Pausewang et al. (6) who have also proposed assignments of some bands empirically. These assignments have been compared with those in other related systems by Sawodny et al. (7).

NORMAL COORDINATE CALCULATIONS

The calculations were set in terms of the FG matrix method (10) using programs similar to those reported by Schachtschneider (11). The X-ray data (12) shows that the ion $[NbOF_5]^{2-}$ has a C_{4v} symmetry. The 15 fundamental vibrations are classified as $4A_1 + 2B_1 + B_2 + 4E$, all of which are Raman active. Only the A_1 and E modes are infrared active. The structural parameters (12) used are - $Nb - F_{eq} = 0.184$ nm, $Nb - F'_{ax} = 0.206$ nm and $Nb - O = 0.168$ nm. The interbond angles are 90°. The molecular structure and internal coordinates are depicted in Fig. 1. The internal symmetry coordinates employed were similar to those reported by Shimanouchi and Nakagawa (13).

A modified Urey-Bradley force field was employed using an initial set of force constants transferred from the force fields of $[NbF_6]^-$ (14) and $[UO_2F_5]^{3-}$ (15). The bending force constant H(FNbF), the nonbonded repulsion terms (F---F) as well as the valence force constant f(Nb–F, Nb–F) for the diagonally opposite bonds r_1, r_3 and r_2, r_4 (Fig. 1) were taken from the force field of $[NbF_6]^-$ (14). The repulsion term F(F---F') was taken slightly lower than F(F---F) based on their distances. The term H(FNbO) was taken from the force field of $[UO_2F_5]^{3-}$ ion (15). The values of the force constants were refined in the usual manner iteratively. The coordinate calculations were extended to $[TaOF_5]^{2-}$ ion transferring the force constants from the force field of $[NbOF_5]^{2-}$. They needed only minor adjustments to give a desired agreement between the calculated and observed frequencies. The vibrational spectra reported by Pausewang (6) has been used for the calculations.

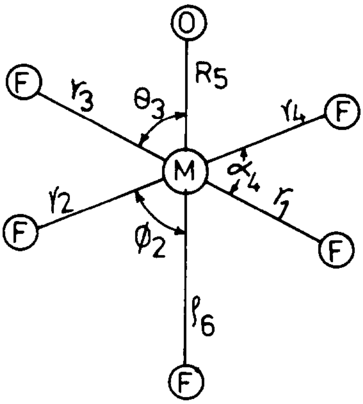

Fig. 1. Structure and representative internal coordinates of the $[MOF_5]^{2-}$ ions.

RESULTS AND DISCUSSION

Force constants The final set of force constants for $[NbOF_5]^{2-}$ and $[TaOF_5]^{2-}$ are shown in Table 1. These values seem reasonable and are similar to the initial ones indicating the good transferability of the Urey-Bradley type force constants for this class of compounds.

TABLE 1

Modified Urey-Bradley force constants (mdyn.$\mathring{A}^{-1}$) for Rb_2NbOF_5 and Cs_2TaOF_5

Force constant	Value	
	Rb_2NbOF_5	Cs_2TaOF_5
K(M—F)	2.15	2.40
K(M═O)	6.50	6.70
K(M—F')	1.05	1.15
H(FMF)	-0.02	0.03
H(OMF)	0.20	0.20
H(F'MF)	-0.02	0.03
F(F---F)	0.46	0.46
F(O---F)	0.12	0.10
F(F'---F)	0.38	0.35
f(M—F, M—F)*	0.44	0.44

* Between the diagonally opposite ones in the equatorial plane.

The value of M—F (M = Nb, Ta) stretching force constants is considerably lower than those observed in hexafluoro metallates (14 This trend is due to the presence of the strong metal-oxygen multiple bond which weakens the M—F bonds (15). The value of Ta—F stretching force constants are slightly higher than the corresponding Nb—F force constants. Such an increase has been noted for the analogous hexafluoro metallates (14).

<u>Spectral interpretation</u> The frequencies of the observed Raman and infrared bands of Rb_2NbOF_5 and Cs_2TaOF_5 are listed in Tables 2 and 3 together with the calculated vibrational frequencies and the potential energy distribution amongst the symmetry coordinates. Most of the fundamental frequencies may be described as pure group vibrations. Some deviation is noted in the calculated values of ν_4 for both $[NbOF_5]^{2-}$ and $[TaOF_5]^{2-}$ ions. Such deviations are also noted in structurally similar species (16,17).

TABLE 2.

Observed and calculated frequencies (cm^{-1}) for Rb_2NbOF_5 and their assignment

Species		Observed		Calculated	Assignment (P.E.D., %)
		R	IR		
A_1	ν_1	918	917	912	ν Nb=O (99)
	ν_2	586	581	584	ν Nb–F (97)
	ν_3	-	410 399	413	ν Nb–F' (90)
	ν_4	266 260	266	237	δ FNbO (84)
B_1	ν_5	-	-	492	ν Nb–F (100)
	ν_6	-	-	200	δ FNbO (100)
B_2	ν_7	289	290 278	289	δ FNbF (100)
E	ν_8	-	536	534	ν Nb–F (98)
	ν_9	310	310 303	308	δ FNbO (81)
	ν_{10}	-	253 247	242	δ FNbF (100)
	ν_{11}	-	210	217	δ FNbO (75)

TABLE 3.

Observed and calculated frequencies (cm^{-1}) for Cs_2TaOF_5 and their assignment

Species		Observed		Calculated	Assignment (P.E.D., %)
		R	IR		
A_1	ν_1	898	896	890	ν Ta=O (100)
	ν_2	595	590	600	ν Ta–F (92)
	ν_3	-	415	415	ν Ta–F' (92)
	ν_4	258	261 256	225	δ FTaO (85)
B_1	ν_5	-	-	512	ν Ta–F (100)
	ν_6	-	-	206	δ FTaO (99)
B_2	ν_7	-	-	318	δ FTaF (100)
E	ν_8	-	520	523	ν Ta–F (99)
	ν_9	310	308	305	δ FTaO (90)
	ν_{10}	-	245	247	δ FTaF (100)
	ν_{11}	205	209	224	δ FTaO (99)

Sawodny and coworkers (7,8) have carried out partial normal coordinate analyses restricted to the stretching vibrations, using valence force functions for $[MOF_5]^{x-}$ where M = Re, Mo, W . The present assignments for $[NbOF_5]^{2-}$ and $[TaOF_5]^{2-}$ are compared with those for similar systems (Table 4). It is satisfactory that most of the assignments for $[NbOF_5]^{2-}$ and $[TaOF_5]^{2-}$ are compatible with the general features of the spectra of oxofluoro metallates and that on the whole, there is consistency in the assignments. The low frequency Raman bands at 162 cm^{-1} and 132 cm^{-1} for Cs_2NbOF_5 have been previously assigned to ν_6 and ν_{11} fundamentals.

TABLE 4.

Comparison of the assignment made for Rb_2NbOF_5 and Cs_2TaOF_5 with those of related compounds

Vibrat-ional mode	$CsMoOF_5$(7)		$CsWOF_5$(7)		$CsReOF_5$(8)		Rb_2NbOF_5		Cs_2TaOF_5	
	IR	R	IR	R	IR	R	IR	R	IR	R
ν_1	973	973	987	989	1002	1005	917	918	896	898
ν_2	662	666	686	689	662	667	581	586	590	595
ν_3	492	-	507	-	535	-	410 399	-	415	-
ν_4	300	-	286	287	281	-	266	266 260	261 256	258
ν_5	-	580	-	594	-	588	-	-	-	-
ν_6	-	-	-	-	-	176	-	-	-	-
ν_7	-	-	-	-	-	-	290 278	289	-	-
ν_8	605	-	608	-	615	614	536	-	520	-
ν_9	-	324	329	331	316	324	310 303	310	308	310
ν_{10}	252	-	242	-	263	-	253 247	-	245	-
ν_{11}	-	-	-	-	-	248	210	-	209	205

However, they need to be reassigned to lattice modes. The frequencies corresponding to ν_6 and ν_{11} are now calculated at 200 cm^{-1} and 217 cm^{-1} respectively, which corresponds to the ir absorption at 210 cm^{-1}.

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