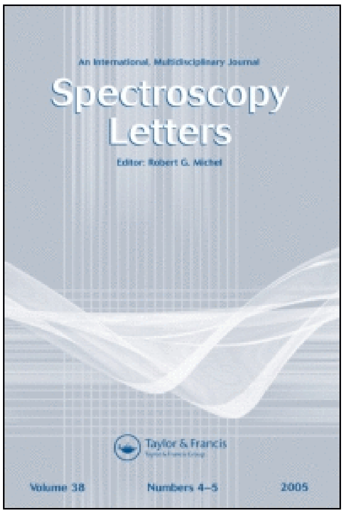

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MOLECULAR CONSTANTS OF MnF_6^{-2} ANION

KEY WORDS: MOLECULAR CONSTANTS

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INTRODUCTION

The normal coordinate analysis of XY_6 type of anions and molecules employing different force fields is well established.[1,2] Recently, the vibrational spectra and complete frequency assignment of MnF_6^{-2} has been reported by Flint.[3] Using the available vibrational data the force constants have been evaluated employing three potential models viz. general valence force field (GVFF), Urey-Bradley force field (UBFF) and orbital valence force field (OVFF). The mean amplitudes of vibration and Bastiansen-Morino shrinkages have also been computed at two temperatures.

Assumming that the anion possesses O_h symmetry, three Raman active modes (ν_1, ν_2 and ν_3), two infrared active modes (ν_3 and ν_4) and one inactive mode (ν_6) are expected for the hexahalide. These normal modes of vibration are theoretically classified as,

$$\Gamma_{vib.} = a_{1g} + e_g + f_{1u} + f_{2g} + f_{2u} .$$

FORCE CONSTANT EVALUATION

Wilson's GF matrix method[4] has been used for the normal coordinate analysis. The kinetic and potential energy matrices have been derived by the standard procedures[4]. Using the symmetry considerations the secular equation $| GF - E\lambda | = 0$ is factorised into a two dimensional and four one dimensional secular equations. For the solution of the inverse eigen value problem of two or higher degree, the number of force constants to be determined exceeds the observed modes. Under this circumstance, several authors[5-7] have proposed mathematical constraints for the evaluation of complete and correct physical force field. Out of these, Fadini's method[6] gives best agreement with the experimentally observed values and Müller's method[7] also gives quite satisfactory results provided that the mass coupling is small.

For the evaluation of the force constants using GVFF, the method of Fadini[6] and method of Müller[7] have been used for the approximate solution of two dimensional equation leading to seven independent force constants. To overcome the difficulty of complete and unique solution of valence force field the simplified force fields viz. OVFF[8] and UBFF[9], have been proposed. In these force fields, the number of vibrational frequencies exceeds the number of force constants. Therefore, the method of least square has been used to adjust the force constants to fit the observed frequencies. A computer programme for an IBM 1620 was used for this purpose. The calculated frequencies using OVFF and UBFF along with the observed frequencies are given in Table 1 and calculated force constants using GVFF, UBFF, and OVFF are given in Table 2.

TABLE 1

OBSERVED AND CALCULATED FREQUENCIES IN cm^{-1}

Anion	Frequency	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
MnF_6^{-2}	Observed	600	510	630	338	308	260
	OVFF	590	501	648	335	312	260
	UBFF	589	504	649	310	338	245

Recently, the vibrational spectra and normal coordinate analysis of MnF_6^{-2} employing GVFF and OVFF have also been reported by Asprey et al.[10] They have used an arbitrary assumption $F_{34} = f_{r\alpha} - f''_{r\alpha} = 0.03$ mdyne/Å resulting in an incorrect set of force constants. From the experimental results of Kim et al.[2] it is clear that F_{34} is not constant for all the hexafluorides, moreover it is generally higher than 0.03 mdyne/Å . Comparing the percentage deviation of stretching (ν_1, ν_2 and ν_3) and deformation (ν_6, ν_4 and ν_5) vibrations our results show an improvement over that of Asprey et al.[10] using OVFF. Our results of UBFF are also encouraging.

TABLE 2

FORCE CONSTANTS IN mdyne/Å

Valence force constants	Muller	Fadini	Force constants	OVFF	UBFF
f_r	3.07	2.93			
f_{rr}	0.19	0.19	K	2.39	2.42
f'_{rr}	0.21	0.35	H or D	0.36	0.14
$f_{r\alpha}-f''_{r\alpha}$	0.28	0.14			
$f_{\alpha}-f'''_{\alpha\alpha}$	0.36	0.37	F	0.38	0.37
$f_{\alpha\alpha}-f''_{\alpha\alpha}$	-0.01	-0.01	F'	0.01	0.01
$f'_{\alpha\alpha}-f'''_{\alpha\alpha}$	-0.13	-0.14			

MEAN AMPLITUDES OF VIBRATION AND BASTIANSEN-MORINO SHRINKAGES

These have been calculated using the secular equation $|\Sigma G^{-1} - \Delta E| = 0$ and Müller's method.[7] Interatomic distance Mn-F is taken as 2.11992 Å.[12] For the expressions of mean amplitudes of vibration u and Bastiansen-Morino shrinkages δ see i.e. Bye et al.[11] The calculated quantities are given in Table 3.

TABLE 3

MEAN AMPLITUDES OF VIBRATION u IN Å AND BASTIANSEN-MORINO SHRINKAGES δ IN Å

Distances and quantities	$T = 0^{\circ}K$	$T = 298^{\circ}K$
u(X - Y)	0.0449	0.0455
u(Y...Y short)	0.0685	0.0833
u(Y...Y long)	0.0574	0.0621
δ(Y...Y short)	0.00061	0.00091
δ(Y...Y long)	0.00085	0.00125

The calculated results show - u(X-Y) < u(Y..Y long) < u(Y...Y short) and δ(Y...Y short) < δ(Y...Y long) at both the temperatures and increase with it.

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