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NORMAL COORDINATE TREATMENT OF LANTHANIDE HEXAHALIDE ANIONS (LnX_6^{3-})[†]

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CONTENTS

A. INTRODUCTION

Hexahalide complexes of the lanthanide metals have been prepared[1-4] in the form $(RH)_3LnX_6$, where RH represents the pyridinium, triphenyl-phosphonium or tetrabutylammonium cation. The lanthanide hexahalide anion, LnX_6^{3-}, is six-coordinate and believed to occupy a local site of near-octahedral symmetry in the crystalline state[1-4]. These six-coordinate complexes are particularly interesting since lanthanide metals tend to go to higher coordination numbers (e.g. 8, 9, 10 or 12) in other complexes. In a previous paper the far-infrared and Raman skeletal vibrations of the LnX_6^{3-} anion have been determined[4]. These vibrational data for the $(pyH)_3LnX_6$ complexes have been used to perform normal coordinate treatments by assuming five different potential fields. The force constants determined indicate several behavioral trends occurring within the series. Ferraro and coworkers recently presented a complete survey of metal hexahalide systems as studied using these five force fields[5], indicating that no theoretical work or force constants were previously available for any lanthanide hexahalide units with the exception of $CeCl_6^{2-}$.

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TABLE 1

Symmetrized G matrix elements for the octahedral LnX_6^{3-} unit

Symmetry species	G matrix element[a]
A_{1g}	$G_{11} = \mu_x$
E_g	$G_{22} = \mu_x$
F_{1u}	$G_{33} = \mu_x(1 + 2\mu_{Ln}/\mu_x)$
	$G_{34} = -4\mu_{Ln}$
	$G_{44} = 2\mu_x(1 + 4\mu_{Ln}/\mu_x)$
F_{2g}	$G_{55} = 4\mu_x$
	$G_{66} = 2\mu_x$

[a] μ_n = reciprocal mass of n.

B. CALCULATIONS

Computer calculations in this study were performed by an IBM 360–195 or a Sigma V computer. Computer drawings were carried out using a Cal Comp 780 incremental plotter.

C. NORMAL COORDINATE TREATMENT OF LnX_6^{3-}

Normal coordinate treatment of the LnX_6^{3-}anion (where Ln = Nd, Eu, Gd, Dy, Er, Yb and X = Cl, Br) was performed by assuming local octahedral symmetry. All the force fields used here[5-12] have been described in the literature. They are the General Valence Force Field (GVFF), Urey–Bradley Force Field (UBFF), Modified Urey–Bradley Force Field (MUBFF), Orbital Valence Force Field (OVFF) and Modified Orbital Valence Force Field (MOVFF). The elements of the F and G matrices are listed in Tables 1 and 2.

The GVFF contains five force constants. These are $f_r, f_\alpha, f_{rr}, f_{\alpha\alpha}$ and $f_{r\alpha}$, where f_r and f_α are the stretching and bending terms respectively. The remainder are interaction force constants where f_{rr} is the interaction term for two adjacent bonds, $f_{\alpha\alpha}$ for two angles sharing a common bond and in the same plane, and $f_{r\alpha}$ for an angle and a bond included in the angle. The UBFF contains four force constants, where K and H are the stretching and bending force constants and F and F' are repulsion constants between non-bonded atoms. The MUBFF has five independently variable force constants. Three of these are the standard UBFF constants K, H and F. F' is allowed to equal $-\frac{1}{10}F$ as calculated when it is assumed that the forces between non-bonded atoms are proportional to $1/r^9$, where r is the distance between non-bonded atoms. Two additional GVFF-type interaction constants are added. These are the constants h and k, where h is the interaction constant between two angles sharing a common bond and at right angles to each other, and k is the interaction constant for two bonds *trans* to each other. The OVFF has four force constants – K, D, F and F'. These are analogous to UBFF constants except that D is the

TABLE 2

Symmetrized F matrix elements of the octahedral $LnX_6{}^{3-}$unit

UBFF[16]	MUBFF[16,24]	OVFF[25]	MOVFF[5]	GVFF
$F_{11} = K + 4F$	$F_{11} = K + 4F + k$	$F_{11} = K + 4F$	$F_{11} = K + 4F + k$	$F_{11} = f_r + 5.33\, f_{rr}$
$F_{22} = K + F + 3F'$	$F_{22} = K + 0.7F + k$	$F_{22} = K + F + 3F'$	$F_{22} = K + F + 3F' + k$	$F_{22} = f_r - 0.667 f_{rr}$
$F_{33} = K + 2F + 2F'$	$F_{33} = K + 1.8F - k$	$F_{33} = K + 2F + 2F'$	$F_{33} = K + 2F + 2F' - k$	$F_{33} = f_r - 1.33 f_{rr}$
$F_{34} = F + F'$	$F_{34} = 0.9F$	$F_{34} = F + F'$	$F_{34} = F + F'$	$F_{34} = 2f_{r\alpha}$
$F_{44} = H + F/2 - 3/2\,F'$	$F_{44} = H + 0.65F + 2h$	$F_{44} = D/2 + F/2 - 3/2F'$	$F_{44} = D/2 + F/2 - 3/2F'$	$F_{44} = f_\alpha + 2f_{\alpha\alpha}$
$F_{55} = H + 1/2F - 1/2F'$	$F_{55} = H + 0.55F$	$F_{55} = D/4 + F/2 - F'/2$	$F_{55} = D/4 + F/2 - F'/2$	$F_{55} = f_\alpha - 2f_{\alpha\alpha}$
$F_{66} = H + 1/2F + 1/2F'$	$F_{66} = H + 0.45F - 2h$	$F_{66} = D/2 + F/2 + F'/2$	$F_{66} = D/2 + F/2 + F'/2$	$F_{66} = f_\alpha - 2f_{\alpha\alpha}$

TABLE 3

Observed and calculated frequencies and force constants for several lanthanide hexahalide, LnX_6^{3-}, complexes[a]

Hexahalide[b] LnX_6^{3-}		Frequencies (cm^{-1})						Force constants (mdyne/A)					Average percentage deviation	
		$\nu_1(A_{1g})$	$\nu_2(E_g)$	$\nu_3(F_{1u})$	$\nu_4(F_{1u})$	$\nu_5(F_{2g})$	$\nu_6(F_{2u})$	K f_r	F f_{rr}	$H(D)$ f_α	$h(F')$ $f_{\alpha\alpha}$	k $f_{r\alpha}$	(ν_1,ν_2,ν_3)	(ν_4,ν_5,ν_6)
$NdCl_6^{3-}$	Observed	252	204	226	121	113	(80)							
	UBFF	241	193	242	116	121	77	0.69	0.13	0.01	−0.01		5.6	4.9
	MUBFF	246	207	226	116	120	77	0.71	0.11	0.01	0.001	0.11	1.4	4.5
	OVFF	236	194	242	119	116	78	0.71	0.11	0.03	−0.01		6.2	1.7
	MOVFF	245	208	226	120	115	80	0.72	0.10	0.04	−0.01	0.11	1.6	0.8
	GVFF	252	204	226	121	113	80	0.91	0.08	0.08	0.01	0.06	0.0	0.0
$NdBr_6^{3-}$	Observed	154	(123)	167	94	76	(54)							
	UBFF	153	119	172	89	81	52	0.57	0.13	0.01	−0.01		2.3	5.3
	MUBFF	153	123	167	89	81	52	0.58	0.12	0.01	0.001	0.05	0.3	5.2
	OVFF	150	119	174	90	79	54	0.59	0.12	0.03	−0.01		3.5	2.5
	MOVFF	151	125	167	93	77	54	0.60	0.10	0.06	−0.02	0.08	1.2	1.1
	GVFF	154	123	167	94	76	54	0.76	0.07	0.05	0.01	0.04	0.0	0.1
$EuCl_6^{3-}$	Observed	256	(216)	226	144	111	(80)							
	UBFF	243	196	246	125	124	75	0.74	0.12	0.01	−0.02		7.7	10.4
	MUBFF	250	220	226	126	124	75	0.78	0.09	0.03	0.01	0.16	1.3	10.2
	OVFF	234	197	249	133	118	80	0.79	0.09	0.07	−0.02		9.3	4.6
	MOVFF	248	221	228	136	115	80	0.85	0.06	0.10	−0.02	0.19	2.0	3.4
	GVFF[c]	257	216	235	128	112	79	1.02	0.07	0.11	0.02	0.12	1.4	4.3
$EuBr_6^{3-}$	Observed	156	(126)	164	97	81	(57)							
	UBFF	156	119	171	92	86	56	0.57	0.14	0.01	0.01		3.1	4.5
	MUBFF	156	126	164	93	86	55	0.59	0.12	0.02	0.001	0.07	0.1	4.3
	OVFF	154	119	172	94	83	57	0.58	0.13	0.03	−0.01		3.9	2.1
	MOVFF	155	126	164	97	81	57	0.60	0.11	0.06	−0.02	0.09	0.3	0.3
	GVFF	156	126	164	97	81	57	0.79	0.07	0.09	0.01	0.05	0.0	0.1

TABLE 3 (continued)

Hexahalide [b] LnX_6^{3-}		Frequencies (cm^{-1})						Force constants (mdyne/A)					Average percentage deviation	
								K	F	$H(D)$	$h(F')$	k		
		$\nu_1(A_{1g})$	$\nu_2(E_g)$	$\nu_3(F_{1u})$	$\nu_4(F_{1u})$	$\nu_5(F_{2g})$	$\nu_6(F_{2u})$	f_r	f_{rr}	f_α	$f_{\alpha\alpha}$	$f_{r\alpha}$	(ν_1,ν_2,ν_3)	(ν_4,ν_5,ν_6)
$GdCl_6^{3-}$	Observed	258	(202)	227	135	120	(85)							
	UBFF	245	193	242	126	130	81	0.70	0.14	0.01	−0.02		5.4	6.3
	MUBFF	249	206	228	127	130	81	0.71	0.12	0.02	0.003	0.09	1.9	6.2
	OVFF	239	194	243	131	125	85	0.73	0.12	0.05	−0.02		6.0	2.3
	MOVFF	247	207	227	134	123	84	0.74	0.11	0.06	−0.02	0.11	2.2	1.4
	GVFF	258	202	227	135	120	85	0.91	0.09	0.10	0.01	0.04	0.0	0.0
$GdBr_6^{3-}$	Observed	157	(122)	163	90	85	(61)							
	UBFF	156	120	167	88	88	60	0.54	0.15	0.01	−0.01		1.6	2.2
	MUBFF	156	122	163	89	87	60	0.57	0.13	0.02	−0.005	0.04	0.3	1.8
	OVFF	156	120	166	89	85	61	0.54	0.15	0.03	−0.01		1.2	0.5
	MOVFF	157	122	163	90	85	61	0.54	0.15	0.03	−0.01	0.03	0.0	0.0
	GVFF	157	122	163	90	86	61	0.75	0.08	0.09	0.003	0.03	0.0	0.4
$DyCl_6^{3-}$	Observed	257	(198)	230	139	118	(81)							
	UBFF	245	193	242	128	129	77	0.71	0.14	0.006	−0.02		4.0	7.0
	MUBFF	247	203	231	128	129	77	0.70	0.13	0.02	0.006	0.07	2.2	7.2
	OVFF	238	194	243	134	123	81	0.75	0.11	0.05	−0.02		5.1	3.7
	MOVFF	243	204	230	137	122	80	0.76	0.09	0.07	−0.03	0.09	2.8	1.9
	GVFF	257	198	230	139	116	82	0.88	0.09	0.10	0.01	0.02	0.0	0.9
$DyBr_6^{3-}$	Observed	159	(124)	161	94	90	(64)							
	UBFF	158	120	166	92	92	63	0.54	0.16	0.02	−0.01		2.2	1.5
	MUBFF	158	124	161	93	92	63	0.57	0.14	0.02	−0.005	0.06	0.2	1.2
	OVFF	159	120	165	93	90	64	0.53	0.17	0.03	−0.006		2.2	0.4
	MOVFF	161	123	161	94	89	64	0.53	0.16	0.04	−0.01	0.04	0.6	0.5
	GVFF	159	124	161	94	90	64	0.78	0.08	0.10	0.002	0.04	0.0	2.1

TABLE 3 (continued)

		Frequencies (cm^{-1})						Force constants (mdyne/A)					Average percentage deviation	
Hexahalide[b] LnX_6^{3-}		$\nu_1(A_{1g})$	$\nu_2(E_g)$	$\nu_3(F_{1u})$	$\nu_4(F_{1u})$	$\nu_5(F_{2g})$	$\nu_6(F_{2u})$	K f_r	F f_{rr}	$H(D)$ f_α	$h(F')$ $f_{\alpha\alpha}$	k $f_{r\alpha}$	(ν_1,ν_2,ν_3)	(ν_4,ν_5,ν_6)
$ErCl_6^{3-}$	Observed	260	(200)	229	143	118	(81)							
	UBFF	247	193	242	130	130	77	0.72	0.14	0.01	−0.03		4.7	8.4
	MUBFF	248	205	230	130	130	77	0.74	0.11	0.03	0.007	0.08	2.4	8.1
	OVFF	238	195	244	137	124	81	0.77	0.10	0.06	−0.03		5.9	3.3
	MOVFF	244	207	229	140	123	80	0.79	0.09	0.08	0.03	0.11	3.1	2.3
	GVFF	260	220	229	143	116	82	0.90	0.10	0.10	0.02	0.02	0.0	0.9
$ErBr_6^{3-}$	Observed	161	(121)	166	94	90	(64)							
	UBFF	160	121	167	93	93	63	0.55	0.16	0.02	−0.007		0.5	1.9
	MUBFF	160	121	166	93	92	63	0.57	0.16	0.01	−0.005	0.02	0.3	1.6
	OVFF	161	121	166	94	90	64	0.54	0.17	0.03	−0.007		0.2	0.1
	MOVFF	161	121	166	94	90	64	0.54	0.17	0.03	−0.007	0.004	0.1	0.1
	GVFF	161	121	166	94	90	64	0.75	0.09	0.11	0.005	0.02	0.0	0.2
$YbCl_6^{3-}$	Observed	263	(207)	226	139	111	(79)							
	UBFF	245	197	243	123	124	74	0.75	0.13	0.01	−0.02		6.5	9.8
	MUBFF	250	213	227	123	124	74	0.76	0.11	0.02	0.006	0.12	2.7	9.8
	OVFF	234	198	246	131	118	79	0.80	0.08	0.07	−0.02		8.0	4.1
	MOVFF	245	215	226	135	116	78	0.84	0.06	0.09	−0.03	0.16	3.7	2.8
	GVFF	263	207	226	139	111	79	0.96	0.09	0.10	0.16	0.05	0.0	0.2
$YbBr_6^{3-}$	Observed	160	(119)	161	96	78	(55)							
	UBFF	157	118	165	91	84	53	0.56	0.15	0.000	−0.02		1.9	5.9
	MUBFF	156	121	161	91	84	53	0.56	0.14	0.005	0.002	0.03	1.2	5.8
	OVFF	151	118	167	93	82	55	0.58	0.12	0.03	−0.02		3.4	2.9
	MOVFF	152	122	161	94	81	55	0.59	0.11	0.05	−0.02	0.06	2.4	2.0
	GVFF	160	119	161	96	78	55	0.73	0.09	0.19	0.06	0.17	0.0	0.1

[a] Observed frequencies listed in parentheses were derived from combination bands or calculations.

[b] All observed frequencies are those for the solid pyridinium complex, $(pyH)_3LnX_6$.

[c] Oscillating, best fit given.

contribution to the potential energy of $\Delta\beta$. Here $\Delta\beta$ is the angle deformation of the bond M–X away from its idealized hybrid orbital as opposed to $\Delta\alpha$ (of UBFF), which is the angle deformation of XMX. The MOVFF has five force constants. Four are basic OVFF constants (i.e. K, D, F and F') and the fifth is the GVFF-type interaction, k, as defined for MUBFF. The derivation and more detailed discussion of these force fields can be found elsewhere[5–12].

Solutions of secular equations were performed using a program of Yeranos and Foss[13]. A least-squares analysis was employed fitting calculated frequencies to observed experimental frequencies to give a "best" set of force constants. Table 3 gives the results of these calculations. Observed and calculated frequencies, as well as converged force constants are given for each force field. The percentage deviation of the calculated from the observed frequencies are given as an average for ν_1, ν_2 and ν_3 (essentially stretching) and ν_4, ν_5 and ν_6 (essentially bending). The General Valence Force Field values are given as a reference although an artificial problem where the number of knowns is equivalent to the number of unknowns has been created. This is a result of the calculation fixing $\nu_6 = \nu_5/\sqrt{2}$ which is implicit in GVFF assumptions. The result was a "perfect fit" solution for eleven of the twelve complexes for which GVFF calculations were performed. However, no convergence could be achieved for $EuCl_6^{3-}$, and the refinement problem oscillated between two sets of force constants, neither of which gave a "perfect fit", Although several methods of damping the refinement process were tried for $EuCl_6^{3-}$, no convergence could be achieved.

In this paper we assume that the force field giving the lowest average percentage deviation (i.e. best fit of calculated to observed frequencies) is the "best" potential energy force field. For all twelve of the LnX_6^{3-} units studied here, the MOVFF gives the "best" overall fit for both stretching and bending vibrations. MUBFF also gives a "good" fit for the stretching frequencies. However, MUBFF is noticeably bad for those vibrations which are essentially bending (ν_4, ν_5 and ν_6). This is manifest in the higher average percentage deviation for ν_4, ν_5 and ν_6 for MUBFF compared with MOVFF. Previous studies comparing these force fields for octahedral complexes indicate that MOVFF gives best fits with observed frequencies for most hexachlorides and hexabromides[5].

D. FORCE CONSTANTS

It is important to consider the significance of several individual force constants. The metal–halogen stretching force constant (f_r or K) takes the largest value and is most variable among the force constants studied here. Further, this stretching force constant readily lends itself to direct comparison with such properties of the LnX_6^{3-} unit as bond strength, bond length, oxidation number and bond order. This metal–halogen stretching force constant is 0.72–0.79 mdyne/Å for the $LnCl_6^{3-}$ complexes and 0.54–0.59 mdyne/Å for the $LnBr_6^{3-}$ complexes. The lower value for the bromide complexes was expected as

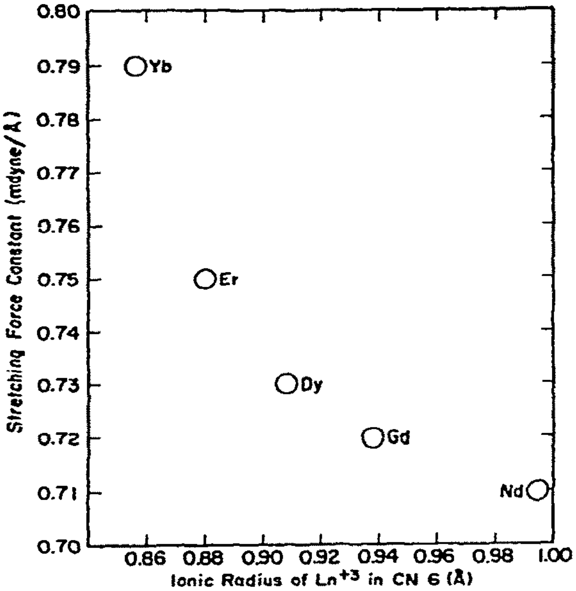


Fig. 1. Variation of the stretching force constant with the ionic radius of the metal for $LnCl_6^{3-}$.

the observed fundamental halide shift can be accounted for only partially by the mass change[4]. In general, the metal–halogen stretching force constant, f_{LnX}, decreases in going from fluorine to iodine[5]. Our results are consistent with these observations. This order may be expected since the lanthanide metals act as Chatt–Ahrland Group A metals[2], so that stronger bonds are formed with lighter halogens (F > Cl > Br > I).

Some variation of the metal–halogen stretching force constant occurs for different metals within the lanthanide series. As the ionic radius of the metal ion decreases by lanthanide contraction (moving towards higher atomic number) the force constant increases indicating a stronger and shorter metal–halogen bond. Figures 1 and 2 show the variation of the stretching force constant with the ionic radius of the Ln^{3+} metal. The force constant (K) plotted is the average of the refined force constant for UBFF, MUBFF, OVFF and MOVFF. The GVFF stretching force constant (f_r) was not included for the reasons discussed earlier. The ionic radii are those given for Ln^{3+} ions by Douglas and McDaniel[14]. Although Ln^{3+} ionic radii, as found in the literature, vary considerably in absolute value the trend observed here is consistent for several different reported radii. The value for $EuCl_6^{3-}$ was not included because it deviated widely and inexplicably from the other values. Figure 1 shows a consistent dependence of the stretching force constant on the ionic radius for the $LnCl_6^{3-}$ complexes. The $LnBr_6^{3-}$ series appears somewhat less consistent (Fig. 2). The bromides seem to be divided into two behavioral groups – one containing Nd and Eu, and one containing the heavier metals such as Gd, Dy, Er and Yb.

All of the force fields considered here, except GVFF, include Urey–Bradley-type repulsions of non-bonded atoms. Steele[15] has pointed out that these interactions occur

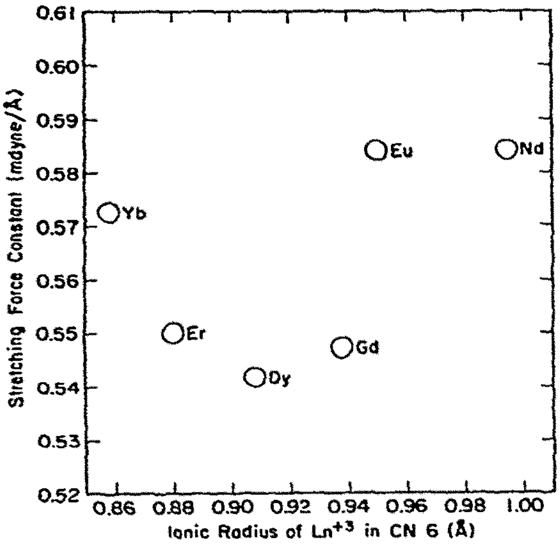


Fig. 2. Variation of the stretching force constant with the ionic radius of the metal for $LnBr_6^{3-}$.

predominantly in systems where steric effects between non-bonded nuclei are significant. We would expect that the lanthanide bromides would demonstrate more steric interactions than the chlorides since bromine is larger than chlorine. In fact, our calculations show larger repulsive force constants, F, for bromides than chlorides. For example, for $GdCl_6^{3-}$, $F_{Cl-Cl} = 0.118$ mdyne/Å and $F_{Br-Br} = 0.145$ mdyne/Å. Further, as the ionic radius of the metal decreases (drawing the halogens closer together), the repulsive force constant, F, tends to increase for the bromides. For example, $NdBr_6^{3-}$, $F_{Br-Br} = 0.118$ m/dyne/Å and for $ErBr_6^{3-}$; $F_{Br-Br} = 0.165$ mdyne/Å. It is rather interesting to note that an opposite trend is seen for the chlorides. $YbBr_6^{3-}$ does not behave consistently. It is, perhaps, worthy of comment that the bromides show smaller average percentage deviations than the chlorides for all the force fields which include Urey–Bradley-type interactions (UBFF, MUBFF, OVFF, MOVFF). This tends to verify Steele's belief that these force fields are most applicable to systems involving large steric interactions[15]. A second explanation for the consistently low percentage deviation for $LnBr_6^{3-}$ calculations (as compared with $LnCl_6^{3-}$) may be that the bromides more closely approach the assumed octahedral symmetry. On the basis of electronic spectra, Ryan[2] draws similar conslusions that the LnX_6^{3-} anion approaches octahedral symmetry in the order I > Br > Cl where $LnCl_6^{3-}$ is the most distorted.

The F' repulsion constant appears in the UBFF, OVFF and MOVFF. In the MUBFF, F' was set equal to $-\frac{1}{10}F$, assuming van der Waal type interactions between non-bonded atoms and covalently bonded molecules. Although the Ln–X bonds of the lanthanide hexahalide anions are somewhat ionic in character, the validity of the $F' = -\frac{1}{10}F$ approximation for LnX_6^{3-} complexes becomes evident when F' is allowed to vary independently of F (that is in UBFF, OVFF and MOVFF); the least-squares refined F' value always converged to very near $-\frac{1}{10}F$ (see Table 3).

Although the stretching interaction force constant k (f'_{rr}) of MUBFF and MOVFF is small, it is obviously highly significant. Both MOVFF and MUBFF give excellent fits for the stretching vibrations. This "good" fit indicates the importance of the interaction between non-adjacent (*trans*) metal–halogen bond stretchings. That is, the metal–halogen stretching vibration has a significant influence on the bond *trans* to it. Such an observation has been expressed previously in terms of the "*trans* effect"[17].

The force constant h of MUBFF is very small for all the molecules studied here. This force constant represents the interaction of adjacent angles sharing a common bond but not in the same plane. The smallness of this force constant and the poor fit for bending fundamentals (large percentage deviation for ν_4, ν_5, ν_6) in MUBFF lead us to conclude that h ($f'_{\alpha\alpha}$) is not an important interaction to be included in the potential energy description of the LnX_6^{3-} system.

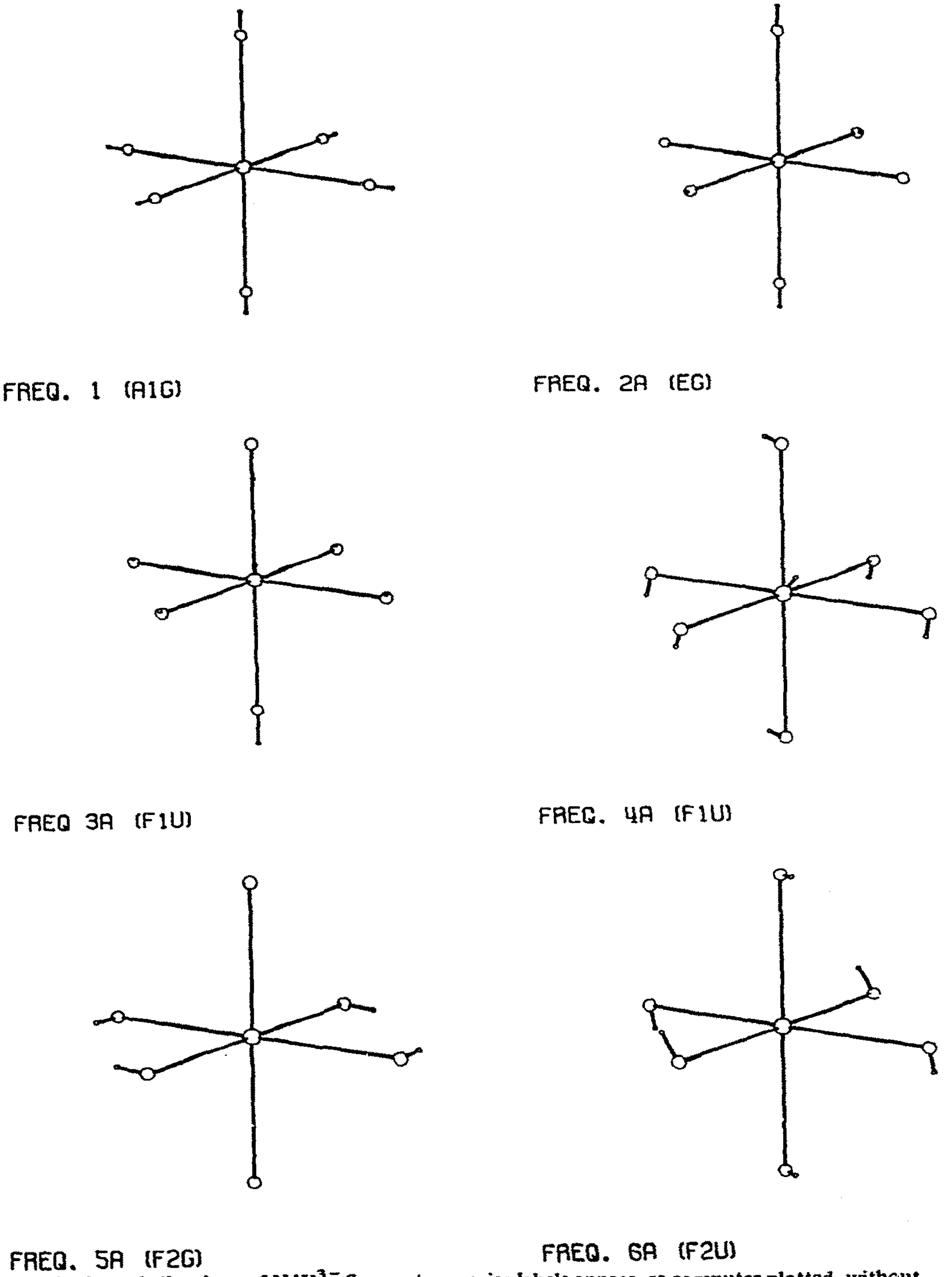
E. POTENTIAL ENERGY DISTRIBUTION

The potential energy distribution coefficient, PED, is defined by

$$\mathrm{PED} = \Lambda^{-1}\ (JZ)\ \Phi$$

where JZ is the Jacobian matrix expressing the variation of the eigen-value with the force constants, Φ is the column force constant matrix, and Λ^{-1} is the reciprocal diagonal matrix of the eigenvalues[19]. The PED has been calculated over the force constants for each of the force fields and LnX_6^{3-}units. The results are not listed for the sake of brevity but are available from the authors on request.

From the PED it is evident that ν_1 and ν_2 are pure stretching modes since these two vibrations include no contribution from the bending constants. The opposite is true for ν_5 and ν_6 which can be considered pure bending modes. Although ν_4 is primarily a bending vibration and ν_3 is largely stretching, a slight amount of coupling between these two modes is seen for some LnX_6^{3-} groups. However, the contribution is usually less then 5% and can be considered nearly insignificant. The importance of the k (f'_{rr}) constant, added to the MUBFF and MOVFF, is evident in the PED only for stretching vibrations. The h ($f'_{\alpha\alpha}$) force constant of MUBFF is insignificant for many of the complex ions, although it does indicate some participation in the ν_4 and ν_6 vibrations of some heavier metal chlorides. The PED of the repulsive force constant, F, is rather interesting. As might be expected, the PED of F tends to be greater for bending modes than for stretching modes. Further, F participation is, in general, larger for the bromides than for the chlorides and increases as the radius of the central metal decreases.



FREQ. 1 (A1G)

FREQ. 2A (EG)

FREQ 3A (F1U)

FREQ. 4A (F1U)

FREQ. 5A (F2G)

FREQ. 6A (F2U)

Fig. 3. Normal vibrations of NdX_6^{3-}. Symmetry species labels appear, as computer plotted, without subscripts, i.e. F1U is equivalent to F_{1u}.

F. CARTESIAN COORDINATE DISPLACEMENTS AND PLOTTING OF NORMAL MODES

The solution of the secular equation provides eigenvalues, PED information and force constants. However, it is rather difficult to visualize the actual vibration from these data. We can plot the molecular motion by transforming the normal mode of vibration into Cartesian coordinate space. The transformation matrix from the normal to Cartesian coordinates can easily be obtained using Schachtschneider's programs[18]. The calculations have been completed using both GVFF and UBFF with no significant changes in the results. The results were plotted using the crystallographer's ORTEP program[19] as described by LaBonville and Williams[20]. Figure 3 shows the resulting normal modes of vibrations. These displacements have been multiplied six times in order to make small displacements observable.

The importance of plotting out the actual normal vibrations for any system becomes apparent when the drawings of Fig. 3 are compared with any theoretical representation of normal vibrations for octahedral symmetry. Several standard texts give the theoretically expected vibration for MX_6 octahedral units[21–23]. Although these are probably correct for the general case, some variations always occur in practice. In this study, the ν_1, ν_2, ν_3 and ν_5 vibrations agree with the standard descriptions of the normal modes. However, ν_4 and ν_6 vary slightly but significantly.

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