UNIQUE FORCE FIELDS OF SOME XY$_6$ TYPE IONS

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ABSTRACT

An attempt has been made to fix the unique force fields of some XY$_6$ type ions through the parametric representation method of Strey[1]. Under the condition stipulated by Strey for non-hydrides of minimum bending force constant, the parameter ϕ in degrees was found to be 61.45, 60.56, 60.32, 60.17, 59.85, 59.21, 54.57, 54.06, 52.83, and 51.24 for $PbCl_6^{2-}$, $PtCl_6^{2-}$, $IrCl_6^{2-}$, $OsCl_6^{2-}$, $ReCl_6^{2-}$, $HfCl_6^{2-}$, $CeCl_6^{2-}$, $TeCl_6^{2-}$, $SnCl_6^{2-}$ and $PdCl_6^{2-}$ ions respectively. Mean amplitudes of vibrations and mean square perpendicular amplitudes[2] of the above listed ions are reported. The molecular constants are in good agreement with those reported by others[3,4].

INTRODUCTION

IN the case of polyatomic molecules the description of general potential field often becomes incomplete because of the excess of potential energy constants over the vibrational frequencies. Therefore to determine a unique set of force constants other sources have to be searched. As a result of this, one has to reduce the force constants as in UBFF[5], HBFF[6], and OVFF[7] or determine mean square amplitudes, mean square perpendicular amplitudes and Coriolis coupling constants which are closely related to the potential energy constants. Several kinematic methods have been employed to a separate potential energy F-Matrix[8,9]. The method of 'Characteristic Set' by Herranz and Castano[10] is interesting because the symmetry force constants are determined without recourse to any assumption regarding the force fields.

The present work deals with the general study of octahedral ions of the type XY$_6$ (X = Pb, Pt, Ir, Os, Re, Hf, Ce, Te, Sn, Pd; Y = Cl) using the parametric method suggested by Strey[1], with a view to fix the force fields.

POTENTIAL ENERGY CONSTANTS

The potential energy matrix F and inverse kinetic energy matrix G are found using the symmetry co-ordinates,

$$F = UfU^*$$

$$G = (UD)(UD)^*$$

where f is the force constant matrix, U is the matrix of transformation from the internal co-ordinates to the symmetry co-ordinates, U^* is its transpose and D is the matrix of the transformation from the mass weighted cartesian to the internal co-ordinates. Asterisk represents the transpose.

In the secular equation,

$$(GF)L = L\Omega \tag{1}$$

of any polyatomic molecule,

$$F = L^{-1*}\Omega L^{-1} \tag{2}$$

where G is the inverse kinetic energy matrix, Ω is the diagonal matrix with $\Omega_i = 4\pi^2 C^2 v_i^2$, v_i being the ith frequency in cm^{-1} and C the velocity of light in cm.sec^{-1}, L^{-1} is the transformation matrix from the symmetry to the normal co-ordinates, L is the inverse of L^{-1} and F is the potential energy matrix.

For the (1×1) species the force constants can be evaluated directly from the observed frequencies using the first degree secular equation, whereas for the case of two-dimensional symmetry species, for a set of vibrational frequencies, the solution of the relation depends on an arbitrary parameter, say ϕ $(0 \leqslant \phi \leqslant 2\pi)$.

For an n-dimensional problem, to get a unique solution for ϕ, $n(n-1)/2$ parameters are necessary. ϕ is so chosen that either f_d exhibits a maximum or f exhibits a minimum depending on the presence of hydrogen in the molecule. From relations (1) and (2) L is found to obey the normalising equation,

$$G = LL^* \tag{3}$$

Here L-Matrix is related to L^*-Matrix by the relation,

$$L = L_0 C \tag{4}$$

where $L_0 = VT^{\frac{1}{2}}$, V being the eigen vector matrix and T the eigen value matrix of G. C is the orthogonal matrix. For $n = 2$, the C-Matrix is given by,

$$C = \begin{vmatrix} \cos\phi & -\sin\phi \\ \sin\phi & \cos\phi \end{vmatrix} \tag{5}$$

Table 1 *Vibrational Frequencies, Parametric Angles and Valence Force Constants* of some XY_6 type ions.*

	Vibrational Frequencies						Parametric Angle ϕ in degrees	f_d	f_{dd}	f_a	Ref.
	v_1	v_2	v_3	v_4	v_5	v_6					
$PbCl_6^{2-}$	281	209	262	142	139	98 3	61.45	1.118	0.123	0.122	a
								1 130	0 120	0.030	b
$PtCl_6^{2-}$	348	318	342	183	171	88.0	60.56	2.038	0.069	0.219	a
								1.910	0 060	0 042	b
$IrCl_6^{2-}$	352	225	333	184	190	134.4	60.32	1.665	0.255	0.227	a
								1.660	0.260	0.060	b
$OsCl_6^{2-}$	346	274	314	177	165	116.7	60.17	1.669	0.186	0.213	a
								1.720	0.140	0.050	b
$ReCl_6^{2-}$	346	275	313	172	159	112.4	59 85	1.719	0.153	0.206	a
								1.710	0.150	0.042	b
$HfCl_6^{2-}$	326	257	275	145	156	80.0	59.21	1.415	0.140	0.154	a
								1.450	0.140	0.047	b
								1.578	0.132	0.201	c
$CeCl_6^{2-}$	295	265	268	117	120	86.0	54.57	1.281	0.059	0.137	a
								—	—	—	
$TeCl_6^{2-}$	301	253	243	139	150	106.1	54.06	1.303	0.093	0.241	a
								—	—	—	
$SnCl_6^{2-}$	311	229	303	166	158	111.7	52.83	1.545	0.154	0.389	a
								1 530	0.150	–	b
$PdCl_6^{2-}$	318	289	346	200	178	125.9	51.24	2.255	0.061	0.718	a
								—	—	—	

a = present work, b = Ref. (3), c = Ref. (4), * = in m.dyne/A

According to Strey[1], the values of the force constants $f_d(\phi)$ and $f(\phi)$ are governed by the relations,

$$\operatorname{Tan}\phi = \frac{\sqrt{T_1}}{\sqrt{T_2}}\frac{V_{12}}{V_{22}} \qquad (6)$$

for hydrides of maximum stretching force constant, and

$$\operatorname{Tan}\phi = \frac{\sqrt{T_2}}{\sqrt{T_1}}\frac{V_{12}}{V_{21}} \qquad (7)$$

for non-hydrides of minimum bending force constant. Here T_1 and T_2 are characteristic values of G and the angle ϕ depends exclusively on the geometry and the atomic masses of the molecule. After fixing the matrix C using the true values of ϕ, L-Matrix is evaluated from (4). Then F-Matrix from (2) becomes,

$$F = L_0^{-1^*}C\Omega C^* L_0^{-1} \qquad (8)$$

The important valence force constants were evaluated from the above equation using the vibrational assignments reported by Theodore *et al*[3].

RESULTS AND DISCUSSION

Taylor[13] has shown that the eigen vector matrix L can be written as $L = L_0 C$ in the parametric form, where L is termed as semi-normal co-ordinate transformation matrix and C is an arbitrary orthogonal matrix containing $n(n-1)/2$ free parameters.

Table 2 *Mean Amplitudes of Vibration (in A) of some XY_6 type ions.*

	$\sigma X-Y$	$\sigma Y-Y$ long	$\sigma Y-Y$ short
$PbCl_6^{2-}$	0.053783	0.066423	0.099096
$PtCl_6^{2-}$	0.069621	0.091740	0.122934
$IrCl_6^{2-}$	0.060297	0.083572	0.098622
$OsCl_6^{2-}$	0.058613	0.073003	0.104934
$ReCl_6^{2-}$	0.058891	0.072828	0.106994
$HfCl_6^{2-}$	0 065104	0.077127	0.116741
$CeCl_6^{2-}$	0.070048	0.077370	0 136315
$TeCl_6^{2-}$	0.076985	0.079312	0.134874
$SnCl_6^{2-}$	0.070041	0.084289	0.119820
$PdCl_6^{2-}$	0.063521	0.071956	0 116028

In the present work, the Rotation method[14] is adopted for L_0. The single parametric angle ϕ in (2 × 2) dimension was evaluated for the 10 ions (table 1). It is interesting to note in the table 1 that the parametric angle ϕ increases with the increase in the atomic weight of the central atom X. The valence force constants thus evaluated are in good agreement with the values reported by others[3,4].

Mean vibrational amplitudes (table 2) and mean square perpendicular amplitudes (table 3) for these ions for various pairs of atomic nuclei were evaluated to check the reliability of the force field model.

Table 3 *Mean Square Perpendicular Amplitudes of Vibration (in A) of some* XY_6 *type ions* (X = Pb, Pt, Ir, Os, Re, Hf, Ce, Te, Sn, Pd; Y = Cl)

	$\langle X-Y \rangle$	$\langle X-Y \rangle$ short		$\langle X-Y \rangle$ long
	$\langle X-Y \rangle$	Δx^2	Δy^2	$\Delta x^2 = \Delta y^2$
$PdCl_6^{2-}$	0.009882	0.006374	0.029344	0.0071073
$PtCl_6^{2-}$	0.010526	0.010503	0.026030	0.010556
$IrCl_6^{2-}$	0.005946	0.007582	0.014195	0.005827
$OsCl_6^{2-}$	0.007424	0.007538	0.018638	0.007605
$ReCl_6^{2-}$	0.007907	0.007688	0.020028	0.008162
$HfCl_6^{2-}$	0.012404	0.009774	0.035359	0.008464
$CeCl_6^{2-}$	0.013313	0.011740	0.034008	0.014044
$TeCl_6^{2-}$	0.009521	0.013930	0.022432	0.009124
$SnCl_6^{2-}$	0.008008	0.010801	0.020276	0.008260
$PdCl_6^{2-}$	0.006301	0.008852	0.016097	0.006588

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NEWS

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