Molecular Force Fields of Some Selenium and Telurium Hexahalide Ions

M. N. AVASTHI and M. L. MEHTA

Department of Physics, University of Jodhpur, Jodhpur, India

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Wilson's GF matrix method has been used to evaluate all the seven independent force constants of some XY_6 type ions using Müller's mathematical constraint. Mean amplitudes of vibration and Bastiansen-Morino shrinkages have also been calculated for these ions.

1. Introduction

XY_6 type molecules and ions, generally are found to possess O_h symmetry or are most likely to possess it [1]. Group theoretical considerations lead to the fact that the symmetry distribution of vibration of these molecules or ions in this point group is given by

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

Out of the six normal modes of vibrations, the three gerade modes $\nu_1(a_{1g})$, $\nu_2(e_g)$ and $\nu_5(f_{2g})$ give rise to Raman active fundamentals; the two ν_3 and $\nu_4(f_{1u})$ modes are the permitted fundamentals in the infrared while the remaining $\nu_6(f_{2u})$ mode is forbidden in Raman effect and infrared. The vibrations ν_1, ν_2 and ν_3 primarily involve stretching of the $X-Y$ bond while the remaining vibrations ν_4, ν_5 and ν_6 are associated with skeletal deformations arising from $Y-X-Y$ bending modes.

Normal coordinate analysis for the molecules and ions of XY_6 type using various force fields, has been made by different workers [2–16]. Recently the fundamental frequencies of $SeCl_6^{-2}$, $SeBr_6^{-2}$, $TeCl_6^{-2}$ and $TeBr_6^{-2}$ ions have been reported by HENDRA and JOVIC [17] and WARE [18] for the first time. These are reported in Table 1. The former authors have also made a normal coordinate analysis using U.B. F.F. It was thought desirable, therefore, to evaluate all the seven force constants with the help of given frequency data for these ions. Naturally the force constants, as evaluated here, must be nearer to the actual values. The present investigation may basically be considered as an extension of the work of HENDRA and JOVIC [17] and an almost full theoretical analysis of the vibrational data.

IONS	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6*	X–Y	Ref.
$SeCl_6^{-2}$	286	257	280	159	165	(117)	2.39	17, 26
$SeBr_6^{-2}$	179	159	225	122	105	(75)	2.54	17, 27
$TeCl_6^{-2}$	289	247	260	150	139	(98)	2.541	17, 18, 28
$TeBr_6^{-2}$	179	159	200	102	105	(75)	2.71	17, 29

Table 1. Fundamental frequencies in cm^{-1} and interatomic distances X–Y in Å.

Using latest available frequency and structural data for these ions the mean amplitudes of vibration and Bastiansen-Morino shrinkages were also calculated.

Reprints request to Dr. M. N. AVASTHI, 807, Chopasani Road, *Sardarpura (Jodhpur), India.*

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* In order to determine the inactive fundamental ν_6, Wilson's rule (mentioned on page 1125 in Ref. [4]) has been applied in our calculation and these calculated values are given in parentheses. It may be added that ν_6 calculated, using UBFF, was the same as got by Wilson's rule.

2. Evaluation of Force Constants

Within the framework of Wilson's GF matrix method [19], the normal coordinate analysis has been carried out. The first problem involved in the evaluation of the force constants is the choice of the suitable set of symmetry coordinates. These coordinates are the linear combinations of the internal coordinates of the molecules or ions concerned. These internal coordinates usually are the bond length displacements Δr_i and the internal bond displacements $\Delta \alpha_{ij}$ $(i \neq j)$. The symmetry coordinates belonging to each representation must be normalized and orthogonalized as well. In our investigation these are the same as used by PISTORIUS [6]. The next step is the choice of a suitable force field. In general, it resolves itself to the use of either the general quadratic function or a Urey Bradley type potential [20]. We have used the former which is given by the expression

$$2V = \sum_i F_i S_i + 2 \sum_{j>i} \sum_i F_{ij} S_i S_j ,$$

where F_i are the valence type force constants, S_i are the valence type internal displacement coordinates and F_{ij} are the interaction constants. The G and F matrix elements used in our work are as follows:

For a_{1g} type vibration:

$$G_{11} = \mu_y , \qquad F_{11} = f_r + 4 f_{rr} + f'_{rr}.$$

For e_g type vibration:

$$G_{11} = \mu_y , \qquad F_{11} = f_r - 2 f_{rr} + f'_{rr}.$$

For f_{1u} type vibration:

$$G_{11} = 2\mu_x + \mu_y , \qquad F_{11} = f_r - f'_{rr},$$

$$G_{12} = G_{21} = 4\mu_x , \qquad F_{12} = F_{21} = -2(f_{r\alpha} - f''_{r\alpha}),$$

$$G_{22} = 8\mu_x + 2\mu_y , \qquad F_{22} = f_\alpha + 2 f_{\alpha\alpha} - 2 f''_{\alpha\alpha} - f'''_{\alpha\alpha}.$$

For f_{2g} type vibration:

$$G_{11} = 4\mu_y , \qquad F_{11} = f_\alpha - 2 f'_{\alpha\alpha} + f''_{\alpha\alpha}.$$

For f_{2u} type vibration:

$$G_{11} = 2\mu_y , \qquad F_{11} = f_\alpha - 2 f_{\alpha\alpha} + 2 f''_{\alpha\alpha} - f_{\alpha\alpha'},$$

here μ_x and μ_y are reciprocals of atomic masses of metal and halide atoms respectively. The valence force constants used here are: f_r – the bond stretching constant for the metal-halide bond; f_{rr} – the constant for the interaction between a bond being stretched and an adjacent bond; f'_{rr} – the constant for interaction between a bond being stretched and a bond opposite to it; $f_{r\alpha}$ – is the interaction constant between an angle and one of the bond forming it's side; $f''_{r\alpha}$ – is the interaction constant between an angle and a bond in its plane but not forming one of it's sides; f_α – is the bending force constant; $f_{\alpha\alpha}$ – the interaction constant between an angle and an adjacent angle in the same plane; $f'_{\alpha\alpha}$ – the interaction constant between an angle and an angle when one bond is common to both bending pairs and others are oposite; $f''_{\alpha\alpha}$ – the interaction constant between an angle and an angle in the adjacent plane but with no bond in common and $f'''_{\alpha\alpha}$ – the interaction constant between an angle and an angle when bending angles are opposite to each other.

A scrutiny of the above expressions shows that there are more than six independent force constants to be evaluated while using the secular equation $|GF - E\lambda| = 0$. This is precisely what has been done by many of the earlier authors. No reasons have been advanced by them – except that of computational convenience. Further, different authors have made different assumptions which do not allow a comparative study of these force constants for a sequence of similar molecules or ions. It was, particularly, from this point of view of comparative study for a series of XY_6 type molecules and ions that these have been taken up for investigation – out of these some have already been reported [14–16], four are reported in this paper and further work is in progress in this direction.

Very recently, additional mathematical constraints [21–24] have been used to overcome the above mentioned difficulty. Out of all these, to the present authors, MÜLLER's method [25] seems to be most practical for species with a heavy central atom. We have, therefore, used it-leading to a unique evaluation of all the seven force constants. The force constants along with symmetry force constants for the f_{1u} mode are given in Table 2.

3. Trends of Force Constants

(i) The stretching force constants f_r decrease as the Y-atom is changed from chlorine to bromine,

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IONS	Symmetry force constants for f_{1u} mode		f_r	f'_{rr}	f_{rr}	$f_{r\alpha} - f''_{r\alpha}$	$f_{\alpha} - f'''_{\alpha\alpha}$	$f_{\alpha\alpha} - f''_{\alpha\alpha}$	$f'_{\alpha\alpha} - f'''_{\alpha\alpha}$
$SeCl_6^{-2}$	0.984	0.064	1.24	0.25	0.05	0.06	0.14	− 0.00	− 0.00
	0.064	0.136							
$SeBr_6^{-2}$	1.056	0.100	1.17	0.11	0.06	0.10	0.14	0.00	0.01
	0.100	0.150							
$TeCl_6^{-2}$	0.977	0.049	1.20	0.23	0.08	0.05	0.12	0.01	0.01
	0.049	0.137							
$TeBr_6^{-2}$	0.979	0.064	1.14	0.16	0.05	0.06	0.12	− 0.00	− 0.00
	0.064	0.116							

Table 2. Symmetry force constants for f_{1u} mode and force constants (in mdyne/Å).

when the X-atom remains unchanged. The same is true when the Y-atom remains as it is while the X-atom is changed from Se to Te.

These facts are consistent both

a) with the decrease in the electronegativity, as we go from chlorine to bromine, and

b) the internuclear distance involved.

4. Mean Amplitudes of Vibration

Using the latest available fundamentals, the mean amplitudes of vibration have been evaluated from the secular equation $|\Sigma\, G^{-1} - \Delta E| = 0$ at two different temperatures 0 °K and 298 °K. Here Σ is the mean square amplitude matrix, G^{-1} is the inverse of the kinetic energy matrix and Δ_k is related to the observed fundamental (ν_k) according to the expression

$$\Delta_k = \frac{h}{8\,\pi^2\,\nu_k\,c}\,\mathrm{Coth}\,\frac{h\,\nu_k\,c}{2\,K\,T}\,.$$

Utilizing group theory, except for the f_{1u} mode, which led to a two dimensional equation, all other modes led to a one dimensional equation. For the unique solutions, again the method of MÜLLER [25] has been used with great advantage. The calculated values of mean amplitudes of vibration u for X − Y, Y . . . Y short and Y . . . Y long distances are given in Table 3.

The mean amplitudes of vibration have a definite trend for all these ions at both temperatures $- u$(Y . . . Y) short $> u$(Y . . . Y) long $> u$(X − Y) and increase with it.

5. Bastiansen-Morino Shrinkages

The interatomic distances for $SeBr_6^{-2}$, $TeCl_6^{-2}$ and $TeBr_6^{-2}$ ions are known experimentally [27–29] while those of $SeCl_6^{-2}$ ion has been calculated by summing covalent radii [26]. These interatomic distances have been used to evaluate Bastiansen-Morino shrinkages ∂ for the Y . . . Y short and Y . . . Y long distances at 0 °K and 298 °K. These are given in Table 4.

The Bastiansen-Morino shrinkages ∂ for the Y . . . Y long distance are greater than for the Y . . . Y short distance for all the ions at both temperatures and increase with it.

The small but real Bastiansen-Morino shrinkages are added to the experimentally observed nonbonded distances to get real nonbonded distances.

IONS	$T = 0$ °K u(X − Y)	 u(Y...Y) short	 u(Y...Y) long	$T = 298$ °K u(X − Y)	 u(Y...Y) short	 u(Y...Y) long
$SeCl_6^{-2}$	0.0501	0.0723	0.0598	0.0657	0.1171	0.0795
$SeBr_6^{-2}$	0.0453	0.0591	0.0505	0.0674	0.1157	0.0822
$TeCl_6^{-2}$	0.0484	0.0758	0.0605	0.0649	0.1312	0.0814
$TeBr_6^{-2}$	0.0427	0.0604	0.0505	0.0659	0.1208	0.0822

Table 3. Mean amplitudes of vibration u in Å.

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IONS	$T = 0\,°K$ $\partial(Y\ldots Y)$ short	$T = 0\,°K$ $\partial(Y\ldots Y)$ long	$T = 298\,°K$ $\partial(Y\ldots Y)$ short	$T = 298\,°K$ $\partial(Y\ldots Y)$ long
$SeCl_6^{-2}$ *	0.00072	0.0024	0.0018	0.0069
$SeBr_6^{-2}$	0.00070	0.0018	0.0019	0.0069
$TeCl_6^{-2}$	0.00052	0.0022	0.0014	0.0076
$TeBr_6^{-2}$	0.00051	0.0016	0.0019	0.0068

Table 4. Bastiansen-Morino shrinkages effect ∂ in Å.

* The Bastiansen-Morino shrinkages effect for $SeCl_6^{-2}$ are less reliable because the interatomic distance (Se—Cl) is not known experimentally but for the sake of comparison we have calculated here.

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