Vibrational Analysis of $SnCl_4N$ and $SnBr_4N$

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The kinetic constants method is applied to evaluate a fresh set of force constants in case of $SnCl_4N$ and $SnBr_4N$, using recent vibrational frequencies. Certain simplifying considerations involving molecular dynamics are made use of in solving the secular equation. The calculated kinetic and force constants are utilised to evaluate other molecular constants, namely mean amplitudes of vibration, Coriolis coupling constants and centrifugal distortion constants. The calculated mean amplitudes of vibration of the Sn-Br bond ($SnBr_4N$) are within the range of the available experimental values ($SnBr_4$).

Introduction

This is a continuation of our systematic studies on the force constants and other molecular constants using the kinetic constants method [1–5] for $SnCl_4N$ and $SnBr_4N$. The molecules belong to the XY_4Z system of the C_{4v} point group and have twelve normal modes, classified as $3A_1+2B_1+1B_2+3E_2$, all of which are Raman active while A_1 and E_2 are infrared active. The vibrational frequencies, structural parameters and the symmetry co-ordinates used in the present investigation are the same as given in [6, 7].

Evaluation of Kinetic and Potential Constants

The kinetic and potential energies for a vibrating system in Wilson's $F-G$ matrix method are given as $2T=\mathring{S}'G^{-1}\mathring{S}$ and $2V=S'FS$, respectively. A transformation of the above equation leads to

$$2T=\sum_{ij}K_{ij}\mathring{r}_i\mathring{r}_j \quad \text{and} \quad 2V=\sum_{ij}F_{ij}r_ir_j,$$

where K_{ij} and F_{ij} are the kinetic and potential energy matrix elements, respectively.

The elements of the kinetic energy matrix are utilised to obtain the kinetic constants. Due to the marked similarity between K_{ij} and F_{ij}, the kinetic constant matrix elements are considered to have the same format as the potential energy matrix elements.

The procedure adopted in obtaining the force constants is as follows: For $2B_1$ symmetry species (2×2 vibrational problem) the basic relations are

$$F_{44}G_{44}+2F_{45}G_{45}+F_{55}G_{55}=\lambda_4+\lambda_5,$$
$$(F_{44}F_{55}-F_{45}^2)(G_{44}G_{55}-G_{45}^2)=\lambda_4\lambda_5.$$

$F_{45}=(K_{45}/K_{55})\ F_{55}$ is used as additional constraint in solving the above secular equations.

In case of $3A_1$ and $3E_2$ symmetry species (3×3 vibrational problem) the secular equations are solved easily by using the following additional constraints.

A_1 Species

$$F_{12}=\left(\frac{K_{12}}{K_{22}}\right)F_{22}, \quad F_{13}=\left(\frac{K_{13}}{K_{33}}\right)F_{33},$$
$$F_{23}=\left(\frac{K_{23}}{K_{33}}\right)F_{33},$$

E_2 Species

$$F_{78}=\left(\frac{K_{78}}{K_{88}}\right)F_{88}, \quad F_{79}=\left(\frac{K_{79}}{K_{99}}\right)F_{99},$$
$$F_{89}=\left(\frac{K_{89}}{K_{99}}\right)F_{99}.$$

Thus the kinetic constants method provides a straight forward procedure to evaluate a reasonable set of force constants for these molecules. In case of species where only one element is involved the force constant can be obtained directly using the relation $F_{ii}=\lambda_iK_{ii}$.

Mean Amplitudes of Vibration

The symmetrised mean square amplitude matrices ($\sum$) are obtained for the temperatures 298.15 K and 500 K using Cyvin's [8] relation $\sum=L\Delta L'$. The $\sum s$

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are used to obtain the mean amplitudes of both bonded and non-bonded atom pairs.

Coriolis Coupling Constants

The Coriolis coupling constants for the molecules under study are treated theoretically. The non-vanishing elements of ζ^α are obtained by applying Jahn's rule [9]. They are of the type ζ^x and ζ^y arising out of the combinations of $A_1 \times E_2$, $B_1 \times E_2$ and $B_2 \times E_2$ and ζ^z due to $B_1 \times B_2$ and $E_2 \times E_2$. The C_{ij} matrix elements are obtained from S vectors by the method of Meal and Polo [10]. The Coriolis coupling constants matrix ζ^α is related to C_{ij} by $\zeta^\alpha = L^{-1} C^\alpha (L')^{-1}$.

Centrifugal Distortion Constants

Cyvin et al. [11] have reformulated the theory of centrifugal distortion by introducing certain new elements $T_{\alpha\beta,s}$ instead of the partial derivatives of the inertia tensor components $J_{\alpha\beta,s}$ of Kivelson and Wilson [12]. The quantities $t_{\alpha\beta\gamma\delta}$ are obtained using the relation $t_{\alpha\beta\gamma\delta} = T' \theta T'$, where $\theta = G^{-1} F^{-1} \cdot G^{-1}$, and hence the τ values are evaluated.

Results and Discussion

The evaluated kinetic and force constants are presented in Tables 1 and 2, respectively. From Table 1 it is observed that the kinetic constants in general increase as the mass of the system increases. Also from Tables 1 and 2 it can be noted that the stretching kinetic constant K_d increases as the mass of the Y atom increases whereas the stretching force constant f_d shows a reverse trend. The decrease in the stretching force constant f_d is in accordance with the decrease in the electronegativity and increase in the atomic radii from Cl to Br. In Table 2, the values obtained by Risbud et al. [7] are given for comparison.

The calculated values of mean amplitudes of vibration at 298.15 K and 500 K along with the experimentally observed mean amplitude values [13] in case of $SnBr_4$ at 296 K are reported in Table 3. It is observed that the calculated values are within the range of the experimental values. From the table it is also observed that the mean amplitudes increase with increase in temperature. The values of the mean amplitude of vibration are useful for the electron diffraction studies of these molecules.

Table 1. Kinetic Constants (amu).

Kinetic Constants	$SnCl_4N$	$SnBr_4N$	Kinetic Constants	$SnCl_4N$	$SnBr_4N$
K_D	13.2956	13.5784	$K_{\alpha\alpha}$	1.5793	0.2708
K_d	29.9616	61.1328	K_β	12.0830	16.3985
K'_{dd}	5.4994	18.8672	$K'_{\beta\beta}$	6.9284	10.9988
K_α	12.0237	20.5415	$K_{\alpha\beta}$	− 0.6830	− 0.8483

$K_{dd} = 0$.

Table 2. Force Constants (m dyn/Å).

Force Constants	$SnCl_4N$	$SnBr_4N$	Force Constants	$SnCl_4N$	$SnBr_4N$
f_D	0.4481 (0.4475)	0.4481 (0.4475)	f_α	0.1435 (0.1371)	0.1331 (0.1201)
f_d	1.6846 (1.6801)	1.3967 (1.3591)	$f_{\alpha\alpha}$	− 0.0093 (− 0.0123)	− 0.0060 (− 0.0138)
f_{dd}	0.1548 (0.1555)	0.1219 (0.1226)	f_β	0.1748 (0.1562)	0.0972 (0.0953)
f'_{dd}	0.2182 (0.2226)	0.2429 (0.2794)	$f'_{\beta\beta}$	0.0812 (0.0983)	0.0576 (0.0587)
			$f_{\alpha\beta}$	− 0.0124 (0.000049)	− 0.0062 (0.000027)

Values in parenthesis are from Ref. [7].

Table 3. Mean amplitudes of vibration (Å).

	$SnCl_4N$		$SnBr_4N$	
	298.15 K	500 K	298.15 K	500 K
$X-Y$	0.0548	0.0673	0.0588 (0.0530)	0.0741
$X-Z$	0.1022	0.1280	0.1012	0.1267
$Y \ldots Y$	0.1132	0.1426	0.1445 (0.110 ± 0.02)	0.1852
$Y \ldots Z$	0.1736	0.2209	0.1846	0.2358

The values in parentheses are experimental values at 296 K in case of $SnBr_4$ (Ref D. A. Long and E. A. Seibold, Trans. Faraday Soc. **56**, 1105 [1960]).

The presently evaluated Coriolis coupling constants are listed in Table 4. From the table it is seen that the sum rule $(\zeta^z_{4,6}) + (\zeta^z_{5,6})^2 = 1$ is satisfied for both molecules. The following relations are also found to hold good:

$$\zeta^x_{A_1\times E_{2a}} = \zeta^x_{A_1\times E_{2b}} = \quad \zeta^y_{A_1\times E_{2a}} = \quad \zeta^y_{A_1\times E_{2b}},$$
$$\zeta^x_{B_1\times E_{2a}} = \zeta^x_{B_1\times E_{2b}} = -\zeta^y_{B_1\times E_{2a}} = -\zeta^y_{B_1\times E_{2b}},$$
$$\zeta^x_{B_2\times E_{2a}} = \zeta^x_{B_2\times E_{2b}} = \quad \zeta^y_{B_2\times E_{2a}} = -\zeta^y_{B_2\times E_{2b}}.$$

The Coriolis coupling constants are useful in vibration-rotation interaction studies of these molecules.

Table 5. Centrifugal distortion constants (kHz).

τ elements	$SnCl_4N$	$SnBr_4N$
$\tau_{xxxx} = \tau_{yyyy}$	− 0.3186	− 0.0616
$\tau_{xzxz} = \tau_{yzyz}$	− 0.0143	− 0.0018
$\tau_{xxzz} = \tau_{yyzz}$	− 0.0707	− 0.0141
τ_{xyxy}	− 0.3587	− 0.0749
τ_{zzzz}	− 0.0476	− 0.0079
τ_{xxyy}	− 0.3186	− 0.0616

The calculated values of the centrifugal distortion constants are given in Table 5. It is observed that the centrifugal distortion constants are very sensitive to the mass of the molecules and decrease as the mass increases. The molecules under study are symmetric rotors, and so the following relations are satisfied among the non-vanishing τ_{elements}:

$$\tau_{xxxx} = \tau_{yyyy}, \quad \tau_{xxzz} = \tau_{yyzz},$$
$$\tau_{xzxz} = \tau_{yzyz}.$$

The centrifugal distortion constants are useful for the microwave spectral analysis of these molecules.

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Table 4. Coriolis Coupling Constants.

Molecule	$A_1 \times E_2$ Coupling								
	$\zeta^x_{1,7a}$	$\zeta^x_{1,8a}$	$\zeta^x_{1,9a}$	$\zeta^x_{2,7a}$	$\zeta^x_{2,8a}$	$\zeta^x_{2,9a}$	$\zeta^x_{3,7a}$	$\zeta^x_{3,8a}$	$\zeta^x_{3,9a}$
$SnCl_4N$	− 0.1660	0.2733	0.6147	− 0.0126	0.0007	− 0.1807	0.5393	− 0.6744	0.2277
$SnBr_4N$	− 0.1935	0.1021	0.6526	0.0069	0.0069	− 0.1197	0.7031	− 0.5872	0.2151
	$B_1 \times E_2$								
	$\zeta^x_{4,7a}$		$\zeta^x_{4,8a}$	$\zeta^x_{4,9a}$		$\zeta^x_{5,7a}$	$\zeta^x_{5,8a}$		$\zeta^x_{5,9a}$
$SnCl_4N$	0.0126		− 0.0007	0.1807		− 0.4534	− 0.6946		0.0118
$SnBr_4N$	− 0.0069		− 0.0069	0.1197		− 0.2543	− 0.6779		− 0.0413
	$E_2 \times E_2$								
	ζ^z_{77}		ζ^z_{78}	ζ^z_{79}		ζ^z_{88}	ζ^z_{89}		ζ^z_{99}
$SnCl_4N$	− 0.2960		0.6474	0.0272		− 0.1023	− 0.0051		− 0.8199
$SnBr_4N$	− 0.6850		0.4419	0.0668		− 0.0111	0.1348		− 0.8222
	$B_2 \times E_2$								
	$\zeta^z_{6,7a}$			$\zeta^z_{6,8a}$			$\zeta^z_{6,9a}$		
$SnCl_4N$	0.0126			− 0.0007			0.1807		
$SnBr_4N$	− 0.0069			− 0.0069			0.1197		
	$B_1 \times B_2$								
	$\zeta^z_{4,6}$			$\zeta^z_{5,6}$					
$SnCl_4N$	1.0000			0.0000					
$SnBr_4N$	1.0000			0.0000					

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