# The Normal Vibrations of Some Silicon Tetrahalides as Calculated by Urey-Bradley Field

By Yuzo KAKIUTI

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Assuming the Urey-Bradley field, Simanouti calculated the normal frequencies of many polyatomic molecules which are in good agreement with the observed values.[1][2][3] In the present paper, the normal frequencies of some silicon tetrahalides were calculated using the similar type of potential field, according to which the potential energy of a molecule can be expressed as follows,

$$V = \sum_i \left[ K'_i r_i \Delta r_i + \frac{1}{2} K_i (\Delta r_i)^2 \right] + \sum_{i<j} \left[ H'_{ij} r^2_{ij} \Delta\alpha_i + \frac{1}{2} H_{ij} (r_i \cdot \Delta\alpha_{ij})^2 \right] + \sum_{i<j} \left[ F'_{ij} q_i \cdot \Delta q_{ij} + \frac{1}{2} F_{ij} (\Delta q_{ij})^2 \right],$$

where the notations same as those given in reference (1) are used. $K$, $H$ and $F$ denote stretching, bending and repulsive force constants, respectively. The values of these force constants were determined so as to give the best fit with the observed frequencies of $SiCl_4$, $SiBr_4$ and $SiI_4$, taking the equilibrium bond distances Si-Cl, Si-Br and Si-I as 2.01, 2.15 and 2.43 A, respectively (see Table 1). Here

Table 1

Values of the force constants ($K$, $H$, $F$, $F' \times 10^{-5}$ dyne/cm and $\kappa \times 10^{11}$ dyne.cm)

| $SiCl_4$ | | $SiBr_4$ | | $SiI_4$ | |
|---|---|---|---|---|---|
| $K$ (Cl) = | 2.59 | $K$ (Br) = | 2.02 | $K$ (I) = | 1.48 |
| $H$ (Cl) = | 0.059 | $H$ (Br) = | 0.051 | $H$ (I) = | 0.044 |
| $F$ (Cl) = | 0.29 | $F$ (Br) = | 0.23 | $F$ (I) = | 0.16 |
| $F'$ (Cl) = | −0.029 | $F'$ (Br) = | −0.023 | $F'$ (I) = | −0.016 |
| $\kappa$ (Cl) = | 0.21 | $\kappa$ (Br) = | 0.18 | $\kappa$ (I) = | 0.14 |

The $\kappa$'s denote the intramolecular tensions.

we assumed that $F'$ value is about −10 % of $F$ value.[4] Some of these values agree very well with those given in reference (3). Using

Table 2

Calculated *vs.* observed frequencies ($cm^{-1}$)

| Class | | Obs.[5] | Calc. | Diff. % |
|---|---|---|---|---|
| $SiCl_4$ | $A_1$ | 424 | 424 | 0 |
| | E | 150 | 150 | 0 |
| | $F_2$ | 221 | 220 | −0.5 |
| | | 610 | 608 | −0.3 |
| $SiBr_4$ | $A_1$ | 249 | 250 | +0.4 |
| | E | 90 | 91 | +1.1 |
| | $F_2$ | 137 | 138 | +0.7 |
| | | 487 | 488 | +0.2 |
| $SiI_4$ | $A_1$ | 168 | 168 | 0 |
| | E | 63 | 63 | 0 |
| | $F_2$ | 94 | 94 | 0 |
| | | 405 | 405 | 0 |
| $SiClBr_3$ | $A_1$ | 159 | 159 | 0 |
| | | 288 | 291 | +1.0 |
| | | 579 | 584 | +0.9 |
| | E | 101 | 102 | +1.0 |
| | | 173 | 162 | −6.4 |
| | | 498 | 491 | −1.4 |
| $SiCl_2Br_2$ | $A_1$ | 111 | 111 | 0 |
| | | 182 | 181 | −0.5 |
| | | 326 | 329 | +0.9 |
| | | 563 | 565 | +0.4 |
| | $B_1$ | 191 (?) | 187 | −2.1 |
| | | 605 | 604 | −0.2 |
| | $B_2$ | 174 | 174 | 0 |
| | | 508 | 494 | −2.8 |
| | $A_2$ | 122 | 123 | +0.8 |
| $SiCl_3Br$ | $A_1$ | 191 | 187 | −2.1 |
| | | 368 | 370 | +0.5 |
| | | 545 | 540 | −0.9 |
| | E | 135 | 134 | −0.7 |
| | | 205 | 206 | +0.5 |
| | | 610 | 606 | −0.7 |
| $SiClI_3$ | $A_1$ | 114 | 117 | +2.6 |
| | | 220 | 228 | +3.6 |
| | | 557 | 570 | +2.3 |
| | E | 73 | 74 | +1.4 |
| | | 134 | 138 | +3.0 |
| | | 411 | 436 | +6.1 |

(1) T. Simanouti, *J. Chem. Phys.*, **17**, 245 (1949).
(2) T. Simanouti, *ibid.*, **17**, 734 (1949).
(3) T. Simanouti, *ibid.*, **17**, 848 (1949).
(4) T. Simanouti, to be published shortly.
(5) M. L. Delwaulle, *J. Phys. Chem.*, **56**, 355 (1952).

| Class | | Obs.[5] | Calc. | Diff. % |
|---|---|---|---|---|
| $SiCl_2I_2$ | $A_1$ | 83 | 83 | 0 |
| | | 160 | 161 | +0.6 |
| | | 276 | 281 | +1.8 |
| | | 538 | 544 | +1.1 |
| | $B_1$ | ? | 165 | |
| | | 589 | 599 | +1.7 |
| | $B_2$ | 149 | 150 | +0.7 |
| | | 418, 436 | 421 | |
| | $A_2$ | 111 | 114 | +2.7 |
| $SiCl_3I$ | $A_1$ | 169 | 165 | −2.4 |
| | | 333 | 333 | 0 |
| | | 519 | 511 | −1.5 |
| | E | 123 | 125 | +1.6 |
| | | 197 | 199 | +1.0 |
| | | 600 | 603 | +0.5 |

the common values of these force constants, the normal frequencies of $SiCl_4$, $SiBr_4$, $SiI_4$, $SiCl_3Br$, $SiCl_2Br_2$, $SiClBr_3$, $SiCl_3I$, $SiCl_2I_2$ and $SiClI_3$ were calculated in the same way as in reference (1), where we assumed that the force constants relating to both unlike halogen atoms $X$ and $Y$ have the average values of two force constants which are concerned with each of them. The results are shown in Table 2. The calculated frequencies are in general in good agreement with the observed values.

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*Faculty of Science,*
*St. Paul's University (Rikkyo Daigaku), Tokyo*