# Orbital Valence Force Field Constants of Tetrachlorides, Tetrabromides and Tetraiodides of Titanium, Zirconium and Hafnium

A. N. PANDEY, D. K. SHARMA, and H. P. MITAL

Department of Phyiscs, Meerut College, Meerut (U.P.), India

The orbital valence force field has been employed to calculate the force constants for tetrachlorides, tetrabromides, and tetraiodides of titanium, zirconium, and hafnium making use of recent vapor-phase Raman spectral data. The results are compared with the Urey-Bradley force constants, and it has been found that these are well comparable. The applicability of the Lennard-Jones potential has been examined to understand the nature of non-bonded interactions. The force constants have also been utilized to study the relative strength of the chemical bonds in tetrahalides and hexahalide anions

Very recently CLARK et al. [1, 2] have studied the Raman spectra of the tetrachlorides, tetrabromides and tetraiodides of titanium, zirconium and hafnium in the vapor-phase. Complete assignments of all the fundamentals, on the basis of tetrahedral symmetry, have been given. They have also reported the thermodynamic functions and force constants for the molecules employing the modified valence force field (MVFF) as well as the Urey-Bradley force field (UBFF). In the present communication it is aimed (i) to apply the orbital valence force field (OVFF) to compute the force constants, (ii) to compare these force constants with the corresponding UBFF force constants, (iii) to discuss the relative stability of the chemical bonds in different molecules, and (iv) to examine the applicability of the Lennard-Jones potential to understand the nature of non-bonded forces.

WILSON's [3] FG matrix method has been used to evaluate the force constants employing OVFF. The expressions for the $F$ and $G$ matrices are taken from KREBS and MÜLLER [4]. For the detail procedure one may refer to [5].

First, all the four OVFF constants; $k_1$, the bond stretching force constant; $k_\alpha'$, the angle distortion constant; $A$ and $B/R$, the interaction constants representing forces between nonbonded atom pairs, were evaluated with the help of four force field equations [4]. The OVFF constants, thus calculated, are presented in Table 1 together with the corresponding UBFF constants [1]. The fundamental frequencies used in these computations are listed in Table 2. It is apparent from Table 1 that the OVFF

constants, $k_1$, $k_\alpha'$, and $A$ are in good agreement with the corresponding UBFF constants, $K$, $3 H$, and $F/2$. As shown in this table, the present calculations lead to a negative value of $B/R$ for most of the molecules. From this it follows that the OVFF model,

Table 1. OVFF constants (in mdyne/Å) for the group IV b tetrahalides. (The values in parentheses indicate UBFF constants $K$, $3 H$, $F/2$ and $-F'$.)

| Halide | $k_1$, $K$ | $k_\alpha'$, $3 H$ | $A$, $F/2$ | $B/R$, $-F'$ |
|---|---|---|---|---|
| TiCl$_4$ | 2.5095 | 0.1185 | 0.0813 | $-$ 0.0098 |
| | (2.509) | (0.105) | (0.0815) | (+ 0.005) |
| | 2.4355 * | 0.0762 * | 0.0906 * | + 0.0139 * |
| TiBr$_4$ | 2.1597 | 0.1453 | 0.0454 | $-$ 0.0152 |
| | (2.150) | (0.126) | (0.0465) | (+ 0.003) |
| | 2.0761 * | 0.1005 * | 0.0558 * | + 0.0085 * |
| TiI$_4$ | 1.6030 | 0.1116 | 0.0448 | $-$ 0.0069 |
| | (1.619) | (0.108) | (0.043) | (+ 0.002) |
| | 1.548 * | 0.0830 * | 0.0517 * | + 0.0079 * |
| ZrCl$_4$ | 2.2961 | 0.0257 | 0.0840 | + 0.0067 |
| | (2.296) | (0.024) | (0.084) | (+ 0.010) |
| | 2.2786 * | 0.0148 * | 0.0862 * | + 0.0132 * |
| ZrBr$_4$ | 2.0953 | 0.1064 | 0.0373 | $-$ 0.0116 |
| | (2.093) | (0.093) | (0.037) | (+ 0.002) |
| | 2.0361 * | 0.0731 * | 0.0447 * | + 0.0068 * |
| ZrI$_4$ | 1.6325 | 0.0882 | 0.0292 | $-$ 0.0085 |
| | (1.627) | (0.075) | (0.030) | (+ 0.003) |
| | 1.5846 * | 0.0623 * | 0.0352 * | + 0.0054 * |
| HfCl$_4$ | 2.369 | 0.0327 | 0.0848 | + 0.0128 |
| | (2.373) | (0.030) | (0.084) | (+ 0.017) |
| | 2.3687 * | 0.0323 * | 0.0848 * | + 0.0130 * |
| HfBr$_4$ | 2.1146 | 0.0664 | 0.0620 | $-$ 0.0036 |
| | (2.117) | (0.060) | (0.0615) | (+ 0.004) |
| | 2.0757 * | 0.0427 * | 0.0668 * | + 0.0102 * |
| HfI$_4$ | 1.8430 | 0.2489 | 0.0029 | $-$ 0.0286 |
| | (1.844) | (0.219) | (0.0025) | (+ 0.002) |
| | 1.7477 * | 0.1942 * | 0.0148 * | + 0.0022 * |

* OVFF constants using Lennard-Jones potential function ($A = 6.5$ $B/R$).

making use of a single term in $B/R$, cannot represent satisfactorily the interaction between non-bonded atom pairs. Negative values of $B/R$ have also been reported in [4, 5].

The force constants are a convenient measure of the strength of a chemical bond and, therefore, it is interesting to study the trend of the force constants among the tetrahalides (except tetrafluoride). The only force constant sufficiently large to warrant discussion is the bond stretching force constant ($k_1$). A comparison of the stretching force constant $k_1$, from Table 1, shows that it decreases in the order $MCl > MBr > MI$ ($M = Ti$, Zr or Hf). The relative strength of the chemical bond must vary in the same order. The interaction consatnt, $A$, follows the same pattern and supports the above conclusion. The variation of the interaction constant is corroborated by the fact that for smaller non-bonded distances its magnitude should be larger, as it happens here [1]. The angle bending force constant, $k_a'$, does not show a regular variation.

The OVFF bond stretching force constants of hexachloride and hexabromide anions [6] with those

of the tetrachlorides and tetrabromides of titanium, zirconium, and hafnium, which possess the same oxidation state [4], are compared in Table 3. From this comparison it is inferred that the chemical bond in the tetrahedral species is stronger than in the octahedral species.

Table 3. Comparison of the bond stretching force constants (in mdyne/Å) of the tetrachlorides and tetrabromides with the hexachloride and hexabromide anions of Ti, Zr, and Hf.

| Halide | $k_1$ | Halide anion | $K$ |
|---|---|---|---|
| $TiCl_4$ | 2.5095 | $TiCl_6^{2-}$ | 0.68 |
| $ZrCl_4$ | 2.2961 | $ZrCl_6^{2-}$ | 1.03 |
| $HfCl_4$ | 2.3690 | $HfCl_6^{2-}$ | 1.12 |
| $TiBr_4$ | 2.1597 | $TiBr_6^{2-}$ | 0.60 |
| $ZrBr_4$ | 2.0953 | $ZrBr_6^{2-}$ | 0.74 |
| $HfBr_4$ | 2.1146 | $HfBr_6^{2-}$ | 0.78 |

In order to understand the nature of the forces acting between the non-bonded atom pairs, a second set of OVFF constants has been calculated by approximating the interaction by a Lennard-Jones potential which includes the dispersion forces. This potential function establishes a relation $A = 6.5\,B/R$ between the non-bonded interaction constants. The set of force constants thus evaluated is included in Table 1. For testing the validity of this approximation these constants, in turn, are employed to calculate the fundamental frequencies. The calculated and observed frequencies are compared in Table 2. It is found that, except $TiBr_4$, the frequencies are not well reproduced. Therefore, it is concluded that for titanium tetrabromide the Lennard-Jones potential is adequate to explain the interaction between non-bond atom pairs while in all other cases it is not a reasonable approximation. To account for these discrepancies Coulomb forces besides dispersion forces should also be taken into consideration as suggested by KREBS and MÜLLER [4].

Table 2. Comparison of the observed and calculated fundamental frequencies (in $cm^{-1}$) for the gorup IV b tetrahalides using OVFF constants from Table 1 with the approximation $A = 6.5\,B/R$.

| Halide | | $\nu_1(A)$ | $\nu_2(E)$ | $\nu_3(F_2)$ | $\nu_4(F_2)$ |
|---|---|---|---|---|---|
| $TiCl_4$ | Obs. | 389 | 114 | 498 | 136 |
| | $A = 6.5\,B/R$ | 389 | 114 | 493 | 152.3 |
| $TiBr_4$ | Obs. | 231.5 | 68.5 | 393 | 88 |
| | $A = 6.5\,B/R$ | 231.5 | 68.5 | 389 | 89.4 |
| $TiI_4$ | Obs. | 162 | 51 | 323 | 67 |
| | $A = 6.5\,B/R$ | 162 | 51 | 321.6 | 72.9 |
| $ZrCl_4$ | Obs. | 377 | 98 | 418 | 113 |
| | $A = 6.5\,B/R$ | 377 | 98 | 417 | 117.6 |
| $ZrBr_4$ | Obs. | 225.5 | 60 | 315 | 72 |
| | $A = 6.5\,B/R$ | 225.5 | 60 | 312.8 | 82 |
| $ZrI_4$ | Obs. | 158 | 43 | 254 | 55 |
| | $A = 6.5\,B/R$ | 158 | 43 | 253.4 | 61.5 |
| $HfCl_4$ | Obs. | 382 | 101.5 | 390 | 112 |
| | $A = 6.5\,B/R$ | 382 | 101.5 | 406.5 | 105.4 |
| $HfBr_4$ | Obs. | 235.5 | 63 | 273 | 71 |
| | $A = 6.5\,B/R$ | 235.5 | 63 | 271 | 78.4 |
| $HfI_4$ | Obs. | 158 | 55 | 224 | 63 |
| | $A = 6.5\,B/R$ | 158 | 55 | 220.3 | 74 |

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