Evaluation of Valance Force Constant for Terahalides Applying the Effective Nuclear Charge Model

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In the present article, the effective nuclear charge model is used to compute the valence force constants for tetrahedral molecules. The experimental force constants determined by normal co-ordinate analysis are compared with the computed results. The agreement between the results, are found to be reasonably good and hence, it is concluded that the said model is successful to predict the approximated valence force constants in complicated polyatomic molecules.

Keywords: Tetrahedral, valance force, nuclear charge.

1. INTRODUCTION

The effective nuclear charge model, developed by Ohwada [1] has been applied to different molecules [2,3] to evaluate the valence force constants in the past. The objective of the present work is to apply the model to compute the valence force constants for tetrahalides. The effective nuclear charges (Zi^*) for the atoms involved in the molecules, are determined from the homo-nuclear diatomic force constants *Kii* [4] and equilibrium intermolecular distance R_{ii} by using the following relation;

$$Z_i^* = \sqrt{\frac{K_{ii} R_{ii}^3}{2}}$$

Also, it is obtained from the stretching force constants available by normal co-ordinate analysis. The calculated valence force constants are summarized in Table 1. The required information such as effective nuclear charges and equilibrium parameters [5,6] are also included in this table.

In the Table 1, K and H stand for stretching and bending force constants respectively. The bond-bond interaction, bond-angle interaction and angle-angle interaction force constants are represented by k, g and h respectively.

Another set of force constants which have been evaluated by the normal co-ordinate analyses, are given in the same Table 1 in bracket for comparison. It is evident from the comparative study of the two sets of force constants (calculated and experimental data)

are moderately under reasonable agreement. To examine the reliability of the calculated force constants given in the Table 1, the vibrational wavenumbers using Wilson's FG-matrix procedure [7]. The computed values are compared with experimentally observed ones [8] as given in Table 2.

Table 1: Experimental and Calculated Valence Force Constants (mdyne /Å) of Tetrahedral Molecules.

Molecule	Z_1	Z_2	R_0	q_o	K	H	k	g	H
CF_4	1.380	1.689	1.320	2.156	6.654 (7.657)	1.534 (0.957)	1.096 (0.524)	0.309 (0.777)	0.438 (0.126)
CCl_4	1.380	1.759	1.766	2.884	2.929 (3.630)	0.695 (0.398)	0.496 (0.263)	0.140 (0.382)	0.198 (0.041)
Cl_4	1.380	1.831	2.150	3.510	1.712 (2.112)	0.418 (0.199)	0.298 (0.086)	0.084 (0.226)	0.119 (-0.001)
SiF_4	2.290	1.689	1.550	2.530	6.018 (6.741)	0.949 (0.435)	0.678 (0.147)	0.192 (0.268)	0.271 (0.087)
$SiCl_4$	2.1424	1.759	2.010	3.280	2.751 (3.328)	0.473 (0.227)	0.338 (0.142)	0.095 (0.182)	0.135 (0.035)
$SiBr_4$	2.1424	1.836	2.150	3.510	2.368 (2.763)	0.420 (0.164)	0.300 (0.029)	0.085 (0.167)	0.120 (0.025)
SiI_4	2.1424	1.831	2.4303	3.970	1.634 (2.028)	0.289 (0.112)	0.206 (0.011)	0.058 (0.124)	0.082 (0.014)
$GeCl_4$	2.3443	1.759	2.113	3.444	2.544 (2.885)	0.408 (0.171)	0.291 (0.129)	0.082 (0.088)	0.117 (0.031)
$GeBr_4$	2.3443	1.836	2.290	3.7395	2.102 (2.351)	0.347 (0.133)	0.248 (0.090)	0.070 (0.103)	0.099 (0.022)
GeI_4	2.3443	1.831	2.500	4.0824	1.610 (1.825)	0.266 (0.092)	0.189 (-0.002)	0.054 (0.085)	0.076 (0.013)
$SnCl_4$	2.7373	1.759	2.281	3.7244	2.289 (2.599)	0.323 (0.106)	0.230 (0.082)	0.065 (0.041)	0.092 (0.021)
$SnBr_4$	2.7373	1.836	2.440	3.9844	1.967 (2.134)	0.287 (0.089)	0.205 (0.062)	0.058 (0.056)	0.082 (0.017)
SnI_4	2.7373	1.831	2.640	4.311	1.548 (1.490)	0.225 (0.068)	0.161 (0.049)	0.046 (0.053)	0.064 (0.012)
TiF_4	2.6852	1.689	1.754	2.864	4.724 (4.791)	0.654 (0.140)	0.467 (0.294)	0.132 (0.071)	0.187 (0.006)
$TiCl_4$	2.6852	1.759	2.170	3.5435	2.617 (2.810)	0.375 (0.097)	0.268 (0.117)	0.076 (0.065)	0.107 (0.003)
$TiBr_4$	2.6852	1.836	2.339	3.8195	2.199 (2.423)	0.326 (0.077)	0.233 (0.037)	0.066 (0.071)	0.093 (0.001)
TiI_4	2.6852	1.831	2.540	4.1477	1.712 (1.887)	0.253 (0.066)	0.181 (0.025)	0.051 (0.068)	0.072 (0.0004)
$ZrCl_4$	2.9299	1.759	2.320	3.7884	2.301 (2.570)	0.307 (0.079)	0.219 (0.133)	0.062 (0.037)	0.088 (0.006)

$ZrBr_4$	2.9299	1.836	2.465	4.0252	2.017 (2.264)	0.279 (0.059)	0.199 (0.047)	0.056 (0.043)	0.079 (0.001)
ZrI_4	2.9299	1.831	2.660	4.3436	1.600 (1.791)	0.220 (0.049)	0.157 (0.025)	0.044 (0.043)	0.063 (0.002)
$HfCl_4$	3.4290	1.759	2.330	3.8048	2.592 (2.657)	0.303 (0.092)	0.216 (0.130)	0.061 (0.026)	0.086 (0.009)
$HfBr_4$	3.4290	1.836	2.450	4.0007	2.342 (2.329)	0.284 (0.068)	0.203 (0.097)	0.057 (0.035)	0.081 (0.003)
HfI_4	3.4290	1.831	2.662	4.3469	1.820 (1.959)	0.219 (0.075)	0.157 (-0.031)	0.044 (0.049)	0.063 (-0.001)

Table 2: Comparative Values of Calculated and Experimental Wave-numbers (cm^{-1}).

Molecule	V1	V2	V3	V4
CF_4	942.427(908)	419.785(435)	1483.533(1283)	665.539(632)
CCl_4	459.977(460)	206.859(214)	953.446(793)	326.636(313)
Cl_4	186.734(178)	084.766(90)	709.635(555)	133.090(123)
SiF_4	847.744(801)	330.232(264)	1000.420(1032)	543.456(389)
$SiCl_4$	424.499(424)	170.552(150)	618.707(610)	285.143(221)
$SiBr_4$	263.495(246)	107.113(85)	540.861(494)	180.658(134)
SiI_4	173.589(166)	70.468(58)	440.571(405)	119.411(90)
$GeCl_4$	404.567(396)	158.516(125)	434.057(459)	225.156(171)
$GeBr_4$	245.902(236)	97.406(75)	341.047(332)	163.046(11)
GeI_4	170.739(156)	67.578(52)	284.471(273)	114.609(77)
$SnCl_4$	377.799(369)	140.956(95)	372.513(408)	218.103(126)
$SnBr_4$	234.226(222)	88.565(59)	278.148(284)	146.687(86)
SnI_4	164.842(148)	62.277(42)	228.377(210)	105.686(163)
TiF_4	739.824(712)	274.183(185)	791.200(793)	440.922(209)
$TiCl_4$	404.656(389)	151.886(114)	495.744(498)	252.384(136)
$TiBr_4$	248.085(232)	94.361(69)	407.638(393)	162.309(88)
TiI_4	173.639(162)	65.989(51)	347.269(323)	114.689(67)
ZrCl4	376.323(377)	137.399(98)	393.266(418)	218.556(113)
ZrBr4	235.641(226)	87.222(60)	305.919(315)	147.396(72)
ZrI4	166.499(158)	61.575(43)	255.590(254)	106.256(55)
HfCl4	393.891(382)	136.512(102)	377.926(390)	202.457(112)
$HfBr_4$	250.333(236)	88.024(63)	273.233(273)	142.314(71)
HfI_4	175.078(158)	61.505(55)	215.614(224)	103.434(63)

3. RESULTS AND DISCUSSIONS

A close look at the data tabulated in Table 2, reveals that the two sets of values are, in general, qualitatively reasonable. The comparative observation leads to conclude that the effective nuclear charge model is useful for prediction of approximate valence force constants. The results shown in Table 1, can be taken as input data in an iterative refinement process. The deviation between calculated and experimental values of the valence force constants, can be attributed to the neglect of the contribution of the term N $(r,R)^3$ in potential energy function and slight uncertainty in the observed wavenumbers.

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