Investigation on the Molecular Structures of Titanium Tetrachloride and Zirconium Tetrachloride by Gas Electron Diffraction

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Introduction

The structures of many metallic tetrachlorides have been studied by a number of workers and it has been proved that their configurations are regular tetrahedrons. The structures of the two chlorides dealt with in the present investigation, have already been determined by Lister and Sutton[1] as Ti−Cl =2.18 ±0.04 Å, Zr−Cl=2.33 ±0.05 Å. It is necessary, however, to obtain the data with experimental errors smaller than those dis- obtained by Lister and Sutton in order to cuss the structures of tetrahalide molecules more thoroughly.

The central atoms in these molecules have comparatively large atomic numbers, and the dimensions of these molecules appear to be so large that the effects of molecular vibrations cannot be ignored in a diffraction experiment. Therefore the effects can be expected to be estimated accurately from diffraction patterns.

It is well known that the physical properties have some regularities among various metallic tetrahalides. Furthermore the similarities between titanium tetrachloride and vanadium tetrachloride have been pointed out by Hildebrand[2] for boiling point, melting point, molar volume and so on. Despite their similarities, the vanadium-chlorine interatomic distance in VCl_4, 2.03 Å[3], is very different from the titanium-chlorine interatomic distance obtained by Lister and Sutton in $TiCl_4$. The present study was carried out in order to determine more accurately the structures of titanium tetrachloride and zirconium tetrachloride.

These interesting problems concerning the physical properties will not be solved until studies are made with respect to the bond character in tetrahalide molecules. In the present paper the force constants calculated on the basis of spectroscopic data are compared with the results obtained by electron diffraction and are discussed for tetrachloride molecules.

Experimental

The diffraction photographs were taken with the apparatus[4] which had hitherto been used. The wavelength of electron beams was about 0.06 Å. The wavelength was calibrated with a gold foil. Titanium tetrachloride was used without heating, since it is a liquid and can easily be evaporated at room temperature. Zirconium tetrachloride was evaporated by heating at about 120°C in a high temperature nozzle[5]. The diffraction photographs obtained were measured as usual by the visual method. The visual curves are drawn in Fig. 1V and Fig. 2V for $TiCl_4$ and $ZrCl_4$ respectively. The observed q values for the maxima and the minima are listed in Table I

TABLE I

THE OBSERVED AND CALCULATED VALUES FOR $TiCl_4$

max.	min.	q_{obs}	q^0_{calc}*	$\frac{q^0_{calc}}{q_{obs}}$	$q^{0.0005}_{calc}$*	$\frac{q^{0.0005}_{calc}}{q_{obs}}$
1		7.60	7.30	(0.961)	7.30	(0.961)
	2	9.95	9.30	(0.935)	9.30	(0.935)
2		12.75	12.30	(0.965)	12.30	(0.965)
	3	15.65	15.65	1.000	15.65	1.000
3		18.65	18.90	1.013	18.85	1.010
	4	20.95	21.30	1.017	21.25	1.014
4		23.05	23.40	1.015	23.10	1.001
	5	26.60	26.40	0.992	26.40	0.993
5		29.60	29.65	1.002	29.60	1.000
	6	33.35	32.75	0.982	33.05	0.991
6		35.35	35.50	1.004	35.40	1.001
7		39.45	40.40	1.024	39.90	1.011
	8	43.60	43.55	0.999	43.60	1.000
8		47.60	46.75	0.982	47.35	0.995
	9	52.95	54.35	1.026	53.45	1.009
9		57.15	57.60	1.007	57.35	1.003
	10	61.70	60.75	0.985	61.55	0.998
10		66.05	68.40	1.035	66.65	1.009
	11	70.95	71.60	1.009	71.20	1.003
11		75.10	74.90	0.997	75.50	1.005
	12	80.60	82.40	1.022	80.40	0.998
12		84.00	85.45	1.017	84.90	1.010
	13	88.30	88.75	1.005	89.40	1.012
13		93.30	91.90	1.015	94.00	1.007
	average			1.007		1.003
	average deviation			0.013		0.005

* These values are those calculated for the model having r(Ti−Cl)=2.18 Å. The suffices 0 and 0.0005 show a values which refer to internal vibrations.

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[1] M.W. Lister and L.E. Sutton, *Trans. Faraday Soc.*, **37**, 393 (1941).

[2] J.H. Hildebrand, *J. Chem. Phys.*, **15**, 727 (1947).

[3] W.N. Lipscomb and G. Whitacker, *J. Am. Chem. Soc.*, **67**, 2019 (1945).

[4] M. Kimura, *Chemical Researches*, **9**, 53 (1951).

[5] M. Kimura and M. Aoki, This Bulletin, **26**, 429 (1953).

* See a later section.

and Table II. In these tables the values in parentheses are considered to have some uncertainties and are not used for a quantitative comparison of the observed values with theoretical ones.

TABLE II

THE OBSERVED AND CALCULATED VALUES FOR $ZrCl_4$

max.	min.	q_{obs}	q^0_{calc}*	$\frac{q^0_{calc}}{q_{obs}}$	$q^{0.0008}_{calc}$	$\frac{q^{0.0008}_{calc}}{q_{obs}}$
2		11.45	11.35	0.991	11.35	0.991
	3	14.85	14.75	0.993	14.75	0.993
3		18.35	18.20	0.992	18.20	0.992
	4	24.40	24.50	1.004	24.35	0.998
4		27.90	27.90	1.000	27.80	0.996
	5	32.00	31.10	0.972	31.60	0.987
5		37.25	37.50	1.007	37.00	0.993
	6	40.95	40.90	0.999	40.80	0.996
6		44.90	44.20	0.984	45.00	1.002
	7	50.00	50.95	1.019	49.55	0.991
7		53.80	54.00	1.004	53.95	1.003
	8	58.15	57.35	0.986	58.10	0.999
8		62.60	63.80	1.019	62.55	0.999
	9	66.60	67.20	1.009	66.80	1.003
9		70.70	70.40	1.004	71.10	1.006
	10	75.25	77.00	1.023	75.40	1.008
10		79.00	80.25	1.016	79.80	1.010
	11	83.40	83.45	1.000	84.05	1.008
11		87.80	86.80	0.989	88.35	1.006
average				1.001		0.999
average deviation				0.011		0.006

* These values are those calculated for the model having $r(Zr-Cl)=2.32$ Å. These suffices 0 and 0.0008 designate a values which refer to internal vibrations.

TABLE III

COMPARISON OF THE CALCULATED VALUES WITH THE OBSERVED VALUES OF $TiCl_4$

$r(Ti-Cl)=2.18$ Å

a	Curve	Average value of q_{calc}/q_{obs}	Average deviation of q_{calc}/q_{obs}
0.0000	T_0	1.007	0.013
0.0004	T_4	1.003	0.007
0.0005	T_5	1.003	0.005
0.0006	T_9	1.003	0.006

TABLE IV

COMPARISON OF THE CALCULATED VALUES WITH THE OBSERVED VALUES OF $ZrCl_4$

$r(Zr-Cl)=2.32$ Å

a	Curve	Average value of q_{calc}/q_{obs}	Average deviation of q_{calc}/q_{obs}
0.0000	T_0	1.001	0.011
0.0007	T_7	0.999	0.007
0.0008	T_8	0.999	0.006
0.0009	T_9	0.998	0.007
0.0010		0.998	0.007_5

The diffraction patterns of both $TiCl_4$ and $ZrCl_4$ show a feature with simple maxima and minima as a whole. A closer examination reveals, however, that the pattern of $TiCl_4$ is characterized by a shelf at the left side of the 7th maximum (designated in Fig. 2 by the 6th maximum) and a shelf perceptible at the right side of the 8th maximum. The pattern of $ZrCl_4$ is charaterized by a shelf at the right side of the 3rd maximum. Therefore these shelves coexistent with the maxima and minima can be expected to lead to the determination of the molecular structures with fair certainty.

(I) Radial Distribution Curve

By use of the visual curves, the radial distribution curves,

$$rD(r)=\sum_q I(q)\exp(-bq^2)\sin(\pi qr/10),$$

were calculated, where b was taken as $\exp(-bq^2_{max})=0.1$. Each curve for $TiCl_4$ and $ZrCl_4$ shows only two peaks, corresponding to the interatomic distances in the tetrahedral molecules with $Ti-Cl=2.18$ Å and $Zr-Cl=2.32$ Å. The radial distribution curves are shown in Fig. 1.

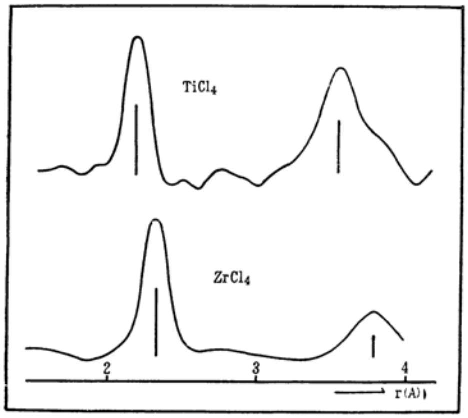

Fig. 1. The radial distribution curves for $TiCl_4$ and $ZrCl_4$.

(II) Theoretical Intensity Curve

The theoretical intensity curves

$$I(q)=\exp(-a_{MCl}q^2)\left[(4Z_MZ_{Cl}/r_{MCl})\sin(\pi qr_{MCl}/10)+6(Z_{Cl}Z_{Cl}/r_{ClCl})\exp(-aq^2)\sin(\pi qr_{ClCl}/10)\right],$$

were calculated for assumed models. Here M designates the central atom, $\exp(-a_{MCl}q^2)$ and $\exp(-aq^2)$ are the factors relating to the molecular vibrations and $a=a_{ClCl}-a_{MCl}$*. Since $\exp(-a_{MCl}q^2)$ is the factor relating only to the damping of curves, it was ignored by being kept constant. A regular tetrahedral form was chosen as a molecular form and the values of r(M-X) at the value obtained from the radial distribution curve were chosen.

Since these molecules have a tetrahedral form, only r(M-Cl) and a are the parameters required to calculate the theoretical intensity curves. The former is related to the position of the maxima and the minima, and the latter is related mainly to the features of the theoretical intensity curves and slightly to the positions of the maxima and the minima.

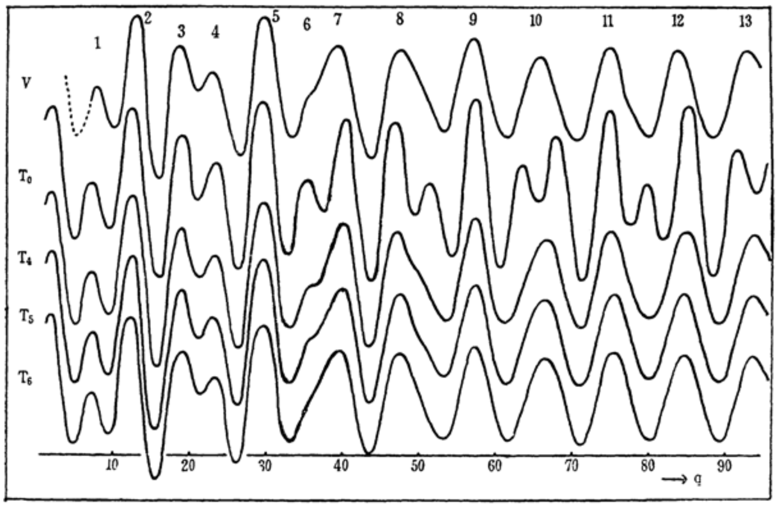

Fig. 2. Visual and theoretical intensity curves for $TiCl_4$. $r(TiCl)=2.18$ Å, $a=0.0000$, 0.0004, 0.0005 and 0.0006 for curve T_0, T_4, T_5 and T_6 respectively.

(i) $TiCl_4$.—The theoretical intensity curves were calculated for the models which have the value of 2.18 Å for $r(Ti-Cl)$ and the values ranging from 0.0000 to 0.0010 for a. Fig. 2 shows that the theoretical intensity curves for $r(Ti-Cl)=2.18$Å. The curve corresponding to $a=0$, i.e. a fixed model, has sharp maxima at the left side of the 7th and 10th maxima and at the right side of the 8th and 11th maxima (Fig. $2T_0$). Accordingly the curve does not agree with the visual curve at all. With the increasing value of a, the theoretical curve becomes similar to the visual curve and is in complete agreement with the visual one in the case of $a=0.0005$ (Fig. $2T_5$). In these curves, the shelf at the right side of the 8th maximum gives an example of noticeable change in the feature with values of a. The shelf disappears at the values of a greater than 0.0006 and is too distinct at those of a less than 0.0004. Thus $a=0.0004-0.0006$ are acceptable values even if experimental errors are taken into consideration. Table I and Table III show a comparison of the theoretical q values for the maxima and the minima in the case of $r=2.18$ Å with the observed ones. As a result, the discrepancies between the observed and the theoretical values were confirmed to be within experimental errors as long as a takes the value in the range 0.0004–0.0006. The errors in our experiments can be considered to be ±0.010 as an average deviation in ratio of the observed values and the calculated ones. Then taking into consideration the average deviations shown in Table III, those in the calculated curves having values other than $r=2.18$ Å and experimental errors, the molecular structure of titanium tetrachloride was obtained to be $Ti-Cl=2.185$ Å ± 0.010 Å, $a=0.0004-0.0006$ and the tetrahedral form.

(ii) $ZrCl_4$.—The theoretical intensity curves were calculated for the models which have the value of 2.32 Å for $r(Zr-Cl)$ and the values ranging from 0.0000 to 0.0011 for a. Fig. 3 shows the theoretical intensity curves for $r=2.32$ Å. The curve corresponding to a fixed model has many shelves (Fig. $3T_0$) and does not agree with the visual curve at all. With the increasing value of a, the shelves disappear except the shelf at the right side of the 3rd maximum and it also becomes indistinct. Upon comparison of these curves with the visual one, it was determined that a takes the values ranging $0.0007-0.0010$ in the case of $r(Zr-Cl)=2.32$ Å by taking into account experimental errors. Furthermore the theoretical curves were compared quantitatively with the visual curve regarding the positions of the maxima and the minima. The results are shown in Table II and Table IV. Then the structure of zirconium tetrachloride was proved to be $Zr-Cl=2.32$ ± 0.01 Å, $a=0.0007-0.0010$ and to have the tetrahedral form by means of a discussion similar to that carried out in the case of titanium tetrachloride.

Mean Amplitudes of Tetrachlorides of 4th Group Elements

The mean-square amplitudes of tetrachlorides of 4th group elements must be calculated from the normal modes of vibrations in order to compare the results obtained from electron diffraction with spectroscopic data. The method of calculation of the mean-square amplitudes of polyatomic molecules was first proposed by Karle and Karle[6]. Since then it has been improved and developed by Morino, Kuchitsu et al.[7]. If the displacements

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[6] J. Karle and I.L. Karle, *J. Chem. Phys.*, **18**, 957 (1950).

[7] a) Y. Morino, K. Kuchitsu and T. Shimanouchi, *J. Chem. Phys.*, **20**, 726 (1952); b) Y. Morino, K. Kuchitsu, A. Takahashi and K. Maeda, *J. Chem. Phys.*, **21**, 1927 (1953).

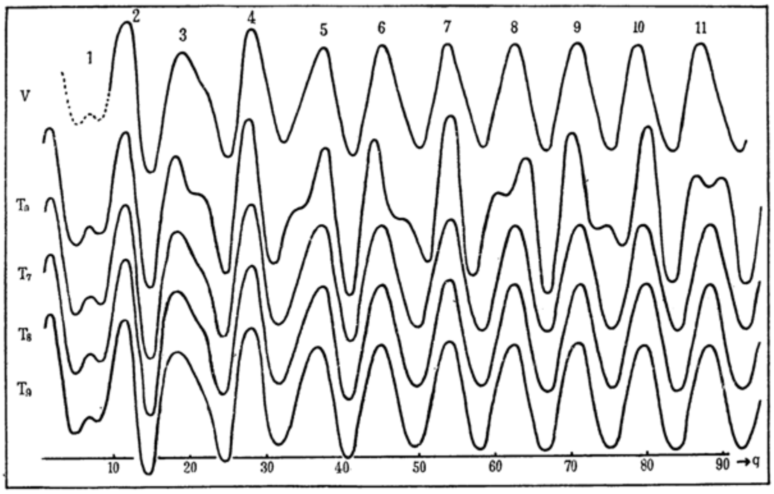

Fig. 3. Visual and theoretical intensity curves for $ZrCl_4$. $r(ZrCl)=2.32$ A, a=0.0000, 0.0007, 0.0008 and 0.0009 for curve T_0, T_7, T_8 and T_9 respectively.

of interatomic distances M-Cl_i and Cl_i-Cl_j are taken as the internal coordinates, and R, $\mathfrak{R}$ and Q represent the matrices of the internal coordinate, the symmetry coordinate and the normal coordinate respectively, these matrices are related to each other by the transformation matrices U' and L as follows,

$$R=U'\mathfrak{R},$$
$$\mathfrak{R}=LQ.$$

Then the mean amplitude $\langle R_i^2\rangle$ can be expressed approximately by the following equation,

$$\langle R_i^2\rangle=kT(U'F^{-1}U)_{ii}+\frac{h^2}{64\pi^2kT}(\mu+\mu').$$

Here F is the potential energy matrix subjected to the symmetry coordinate, F^{-1} is the inverse matrix of F, U' is the transposed matrix of U. The notation μ and μ' signify the reciprocal masses of two atoms associated with the displacement R_i.

The force constants giving the internal potential energy must be determined for obtaining the matrix. The method was studied systematically by Wilson[8] and full studies were reported by Shimanouchi[9] for methane and its derivatives. In the present study the same method was adopted and the potential energy was given by the equation

$$\begin{aligned}V=&h_r r_0\sum_i(\Delta r_i)+(1/2)f_r\sum_i(\Delta r_i)^2\\&+h_q q_0\sum_{i<j}(\Delta q_{ij})+(1/2)f_q\sum_{i<j}(\Delta q_{ij})^2\\&+(1/2)f_\alpha r_0^2\sum_{i<j}(\Delta\alpha_{ij})^2.\end{aligned}$$

The force constants were obtained using the frequencies of the normal modes of vibrations and F matrix was determined. Here r_0, and q_0 are the interatomic distances M-Cl and Cl-Cl in equilibrium. Table V shows the molecular structures used in the calculation, Table VI the frequencies of the normal modes of vibrations, and Table VII the results of the calculation.

TABLE V

THE MOLECULAR STRUCTURES OF TETRA-HALIDES

	$SiCl_4$[10]	$TiCl_4$*	$GeCl_4$[11]	$ZrCl_4$*	$SnCl_4$[11]
M-Cl	2.01	2.18	2.08	2.32	2.30
	regular tetrahedral form				

* The values determined by the present experiment.

TABLE VI

THE FREQUENCIES OF MOLECULAR VIBRATIONS[12]

	ν_1	ν_2	ν_3	ν_4
$SiCl_4$	424	150	608	221
$TiCl_4$	386	120	495	141
$GeCl_4$	396	134	453	172
$ZrCl_4$	?	?	?	?
$SnCl_4$	366	104	403	134

No frequency of the normal modes of vibrations has yet been obtained for $ZrCl_4$. Therefore a method to be mentioned below was used. A plot of the force constant against the atomic number of the central atom yields a straight line approximately for Si, Ge, Sn (Fig. 4). It has already been pointed out[2] that if a plot is made in the same way as mentioned above for the other

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[8] E.B. Wilson, Jr., *J. Chem. Phys.*, **7**, 1047 (1939); **9**, 76 (1941).

[9] T. Shimanouchi, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **22**, 958, 964 (1943); T. Shimanouchi, *J. Chem. Phys.*, **17**, 245 (1949).

[10] K. Yamasaki, A. Kotera, A. Tatematsu, M. Iwasaki, *J. Chem. Soc. Japan*, **69**, 104 (1948).

[11] L. Pauling and L.O. Brockway, *J. Am. Chem. Soc.*, **57** 2684 (1936).

[12] G. Herzberg, "Molecular Spectra and Molecular Structure II, Infrared and Raman Spectra of Polyatomic Molecules", 1949, p. 167.

TABLE VII

FORCE CONSTANTS AND MEAN AMPLITUDE OF MOLECULAR VIBRATIONS

	$SiCl_4$	$TiCl_4$	$GeCl_4$	$ZrCl_4$*	$SnCl_4$
$f_r(\times 10^5$dyn./cm.)	2.597	1.935	2.440	1.800	2.325
$f_\alpha(\times$ 〃)	0.0436	0	0.0442	0	0.0237
$f_q(\times$ 〃)	0.0289	0.294	0.208	0.200	0.118
$h_q(\times$ 〃)	−0.0521	−0.0228	−0.0350	−0.010	−0.0378
$\langle r^2_{\mathrm{MCl}}\rangle$(Å)	0.045	0.049	0.044	0.050	0.045
$\langle r^2_{\mathrm{ClCl}}\rangle$(Å)	0.089	0.108	0.100	0.135	0.120
a_{calc}		0.00045**		0.00094	
a_{obs}		0.0004–0.0006		0.0007–0.0010	

* f and h were determined by the method mentioned in the present paper. a_{calc} is the value calculated using 400°K for T.

** a_{calc} is the value calculated using 300°K for T.

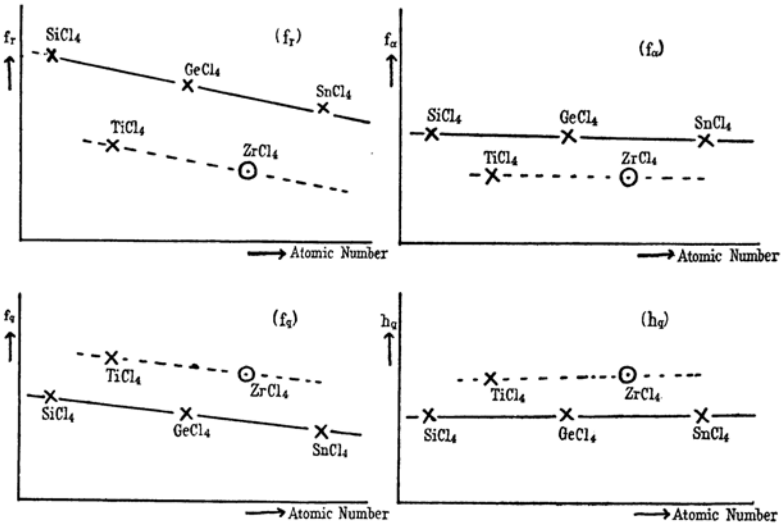

Fig. 4. Force constant of tetrachlorides plotted against the atomic number of central atom in arbitrary unit.

physical properties, the curve for Ti, Hf, Zr and Th runs parallel to that for Si, Ge, Sn and Pb. For the force constants also, a parallelism may be considered to exist between the two series. Therefore a straight line was drawn parallel to that for Si, Ge, Sn and Pb through Ti (Fig. 4). Thus the force constants for $ZrCl_4$ were obtained from the straight line as the values corresponding to atomic number 40 and are listed in Table VII. Although the force constants for a series of Si, Ge, Sn and Pb, rigorously speaking, do not lie on a straight line, f_r for $ZrCl_4$, for example, can be obtained as 1.80 ± 0.03 if the above mentioned parallelism is assumed. Since the mean amplitude depends exceedingly on f_r, such an error in f_r leads to an error of only two or three percent in the mean amplitude even if the errors of the other force constants are taken into account. Consequently the error is less than that involved in an electron diffraction experiment.

The relation between a in $\exp(-a_{ij}q^2)$ and the mean amplitude is expressed by the following equation[13],

$$a_{ij}=\langle r^2_{ij}\rangle\cdot\pi^2/200.$$

Then

$$a=a_{\mathrm{ClCl}}-a_{\mathrm{MCl}}=[\langle r^2_{\mathrm{ClCl}}\rangle-\langle r^2_{\mathrm{MCl}}\rangle]\pi^2/200.$$

a_{calc} was calculated using this equation and is listed in Table VII. The observed values of a are in satisfactory agreement with the calculated ones.

Discussion

The interatomic distances Ti—Cl and Zr—Cl were obtained by us with smaller errors than those obtained by Lister and Sutton. Moreover detailed information was obtained for the molecular vibration from the standpoint of electron diffraction and spectroscopy.

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[13] e.g. P. Debye, *J. Chem. Phys.*, **9**, 55 (1941); R. W. James, *Physik. Z.*, **33**, 737 (1932).

These results can be considered to be accurate enough to be used discussing the molecular structures.

The results obtained above indicate the regular change with the atomic number of the central atom in the molecular vibrations as well as in the metal-chlorine interatomic distances of the tetrahalides of 4th group elements. At the same time the 4th group elements are classified into two groups, Si, Ge, Sn, Pb and Ti, Zr, Hf, Th. Although no detailed statement is made in the present paper, that almost all physical properties are classified into two groups may be interpreted as due to the difference of the bond character between the two groups. The difference of the bond character may be considered to be a necessary consequence arising from the difference of the valence shells between the two groups. Moreover in $TiCl_4$ and VCl_4 the similarity to one another in boiling point, melting point and molar volume, etc. is an example indicating that no physical property depends merely on the geometrical configuration of molecules.

Summary

1) The molecular structures of $TiCl_4$ and $ZrCl_4$ were determined by electron diffraction as follows: $Ti-Cl=2.185 \pm 0.01$ Å in $TiCl_4$ and $Zr-Cl=2.32 \pm 0.01$ Å in $ZrCl_4$, and both molecules have the tetrahedral form. At the same time a in $\exp(-aq^2)$, the term relating to molecular vibrations, was determined. $a_{\mathrm{ClCl}}-a_{\mathrm{MCl}}$ is 0.0004–0.0006 for $TiCl_4$ and 0.0007–0.0010 for $ZrCl_4$.

2) The mean-square amplitudes of $SiCl_4$, $TiCl_4$, $GeCl_4$, $ZrCl_4$ and $SnCl_4$ were calculated using the frequencies of the normal modes of vibrations. $a_{\mathrm{ClCl}}-a_{\mathrm{MCl}}$ thus obtained is 0.00045 for $TiCl_4$ and 0.00094 for $ZrCl_4$. These values are in satisfactory agreement with those obtained by electron diffraction.

3) Almost all physical properties of tetrahalides of the 4th group elements including molecular vibrations are classified into two groups, Si, Ge, Sn and Pb tetrachlorides and Ti, Zr, Hf and Th tetrachlorides. This will be due to the difference in bond character.

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