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## Abstract

## Full Text

*Physical Chemistry*

V. M. TATEVSKII, V. P. SPIRIDONOV, and P. A. AKISHIN

# ON A REGULARITY IN THE INTERATOMIC DISTANCES OF HALIDE MOLECULES OF DIFFERENT GROUPS OF THE PERIODIC SYSTEM OF ELEMENTS\*

*(Presented by Academician A. N. Frumkin, January 4, 1961)*

Earlier, one of us <sup>(4)</sup>, in considering experimental data on the geometry of molecules in the gas phase, concluded that the geometrical configuration of molecules  $AX_n$  (where  $X$  is a halogen) does not change qualitatively when the central atom  $A$  is replaced by an atom of another element  $A'$  from the same group (or subgroup) of the periodic system, provided that the valence, the sequence, and the multiplicity of the bonds characteristic of atom  $A$  are retained for atom  $A'$ . The configuration of  $AX_n$  molecules also does not change when one or several atoms  $X$ , bonded to the given central atom  $A$ , are replaced by other halogen atoms. Therefore molecules of the type  $AX_n$  may be grouped into series of similar molecules in which a definite regularity is found in the values of the interatomic distances.

Fig. 1. Dependence of the interatomic distances  $A-X$  in  $AX_n$  molecules on the ordinal number  $Z$  of the halogen atoms

Let us renumber the groups (subgroups) of the periodic system to which the element  $A$  belongs with the index  $k$ , the elements  $A$  in the  $k$ -th group (subgroup) with the index  $i$  (or  $l$ ), and the elements  $X$  in the halogen group with the index  $j$  (or  $m$ ). Thus, for example, if  $A$  is an atom of an element of the 2nd group, then  $A^{(21)} \equiv \text{Be}$ ,  $A^{(22)} \equiv \text{Mg}$ ,  $A^{(23)} \equiv \text{Ca}$ , etc.; for the halogens  $X^{(1)} \equiv \text{F}$ ,  $X^{(2)} \equiv \text{Cl}$ ,  $X^{(3)} \equiv \text{Br}$ ,  $X^{(4)} \equiv \text{I}$ . Let us fix the group  $k$  and consider the interatomic distances  $A^{(ki)}-X^{(j)}$  in the series of halides  $AX_n$  comprising Table 1, in which the number of rows is equal to the number of elements  $A^{(ki)}$  in the  $k$ -th group (subgroup), and the number of columns to the number of halogens  $X^{(j)}$ . Here there are the following series of similar molecules: series of molecules along the

rows, differing from one another by atoms of the element  $A^{(ki)}$ , and series of molecules along the columns, differing by halogen atoms  $X^{(i)}$ .

\* The present work was carried out by the authors several years ago as part of a broader investigation. During the last three years its results have been used in the course “Structure of Molecules,” taught at the Chemistry Faculty of Moscow University (see also <sup>(1, 2)</sup>). The authors <sup>(3)</sup> have independently arrived at analogous conclusions.

Let us consider the rows of similar halide molecules  $AX_n$  according to the rows of Table 1.

**Table 1**

$A^{(k1)}X_n^{(1)}$	$A^{(k1)}X_n^{(2)}$	$A^{(k1)}X_n^{(3)}$	$A^{(k1)}X_n^{(4)}$
.....	.....	.....	.....
$A^{(ki)}X_n^{(1)}$	$A^{(ki)}X_n^{(2)}$	$A^{(ki)}X_n^{(3)}$	$A^{(ki)}X_n^{(4)}$
.....	.....	.....	.....
$A^{(kl)}X_n^{(1)}$	$A^{(kl)}X_n^{(2)}$	$A^{(kl)}X_n^{(3)}$	$A^{(kl)}X_n^{(4)}$
.....	.....	.....	.....

Figure 1 gives graphs of the dependence of the interatomic distances  $A-X$  in molecules of halides of Groups 1-4 on the ordinal number  $Z_j$  of the halogen atoms\*. In this way one obtains a family of graphs having approximately the same form. Analogous graphs are obtained for halides of elements of other groups of the periodic system. Evidently, the dependence of the interatomic distances  $A-X$  in these molecules on the ordinal number of the halogen atoms can approximately be expressed through a certain function having one and the same form for all rows, and a set of constants. Namely, for the interatomic distances  $A^{(ki)}-X^{(j)}$  in these rows one may write

$$\begin{aligned}
 r_{1j}^{(k)} &= a_1^{(k)} + b_1^{(k)} \varphi^{(k)}(z_j), \\
 &\dots \dots \dots \\
 r_{ij}^{(k)} &= a_i^{(k)} + b_i^{(k)} \varphi^{(k)}(z_j), \tag{1} \\
 &\dots \dots \dots \\
 r_{lj}^{(k)} &= a_l^{(k)} + b_l^{(k)} \varphi^{(k)}(z_j)
 \end{aligned}$$

where  $\varphi^{(k)}(z_j)$  is a function the same for all rows. Obviously, for all such rows, differing in the atoms  $A^{(ki)}$ , according to (1) we shall have

**Fig. 2.** Regularity in the values of interatomic distances  $A-X$ :  $a$ —for halides of elements of Group 1 (along the abscissa are plotted interatomic distances in cesium halides),  $b$ —for halides of elements of Group 2 (along the abscissa are plotted interatomic distances in calcium halides),  $c$ —for halides of elements of Group 4 (along the abscissa are plotted interatomic distances in germanium halides)

$$\varphi^{(k)}(z_j) = \frac{r_{ij}^{(k)} - a_i^{(k)}}{b_i^{(k)}} = \frac{r_{lj}^{(k)} - a_l^{(k)}}{b_l^{(k)}}, \quad (2)$$

whence

$$r_{ij}^{(k)} = c_{il}^{(k)} r_{lj}^{(k)} + d_{il}^{(k)}, \quad (3)$$

where  $c_{il}^{(k)}$  and  $d_{il}^{(k)}$  do not depend on  $j$ , i.e. the interatomic distances  $A^{(ki)}-X^{(j)}$  of molecules of the  $i$ -th row of Table 1 can be represented as a linear function of the interatomic distances of molecules of the  $l$ -th row.

If we consider the rows of molecules  $AX_n$  by the columns of Table 1, then analogously one can obtain the equation

$$r_{ij}^{(k)} = c'_{mj}{}^{(k)} r_{im}^{(k)} + d'_{mj}{}^{(k)}, \quad (4)$$

\* The interatomic distances  $A-X$  for halides of elements of Group 1 are taken from a microwave study (5), with values for the fluorides of lithium, sodium, potassium, and rubidium estimated in that work by a semiempirical formula; for halides of elements of Group 2, and also for the halides of lithium, lanthanum, and neodymium, from electron-diffraction studies (6, 7); for the remaining halides, from (8).

i.e., the interatomic distances  $A^{(ki)}-X^{(j)}$  of the molecules of the  $j$ -th column of Table 1 can be represented by a linear function of the interatomic distances of the molecules of the  $m$ -th column.

The regularity noted can be illustrated graphically (Fig. 2) for halides of different groups of the periodic system (see in more detail (1,2)).

Thus, in the indicated series of halides  $AX_n$ , an approximately linear dependence of the interatomic distances  $A-X$  is realized. Since in these series the sequence and multiplicity of the  $A-X$  bonds are analogous and the valence state of the central atoms  $A$  is the same, the regular change in the interatomic distances  $A-X$  in such series is explained by the periodic change in the properties of the atoms of the elements of one group (or subgroup) of the periodic

system, i.e., this regularity is based on D. I. Mendeleev's periodic law. Periodicity in the properties of molecules was used by D. I. Mendeleev<sup>(9)</sup> to predict a number of properties (for example, specific gravity, boiling point, etc.) of compounds of elements not yet discovered. To find these properties, the arithmetic mean was taken of the corresponding properties of the compounds of elements standing in the periodic table to the right and left, above and below the given element, i.e., in fact a linear dependence on the atomic number of the element was assumed. Subsequently, attempts were made repeatedly to use the periodic law to determine the properties of a series of compounds from the analogous property of another series of compounds. In the Soviet Union this method was developed in the works of V. A. Kireev<sup>(10,11)</sup>, and in recent years in the works of M. Kh. Karapet'yants<sup>(12-15)</sup>.

One special case of the regularity discussed above is of interest. Obviously, if in equation (1) the coefficients  $b_i^{(k)}$  are equal for all atoms of the elements  $A^{(ki)}$ , i.e.  $b_i^{(k)} = b_l^{(k)}$ , then equation (3) takes the form:

$$r_{ij}^{(k)} = r_{lj}^{(k)} + a_i^{(k)} - a_l^{(k)}. \quad (5)$$

Since  $a_i^{(k)}$  and  $a_l^{(k)}$  do not depend on the index  $j$ , it follows from equation (5) that the differences of the interatomic distances  $A^{(ki)} - X^{(j)}$  for two series of similar molecules differing in the atoms  $A^{(ki)}$  do not depend on which halogen atoms the atoms of the elements  $A^{(ki)}$  are bonded to. Consequently, under these conditions, certain effective constant radii can be assigned to the atoms  $A^{(ki)}$ . Completely analogous reasoning can also be carried out for the halogen atoms  $X^{(j)}$ .

Thus, in the special case, effective atomic radii, constant within the considered set of series of molecules, may approximately be introduced in the series of molecules examined; their sum will be equal to the corresponding interatomic distance. The exposition is illustrated by Table 2 for molecules of alkali-metal halides; consideration of it shows that the corresponding differences remain constant with a maximum deviation from the mean of  $\pm 0.03-0.04$  Å. Consequently, the interatomic distance in these molecules can be represented with sufficient accuracy as the sum of certain constant effective atomic radii.

However, the equations given above do not make it possible to determine the numerical values of the effective atomic radii, since the number of independent equations is one less than the number of unknowns. Therefore, in constructing a system of effective atomic radii, additional assumptions must always be introduced. This leads to the necessity, when estimating interatomic distances in unstudied molecules with the aid of effective radii, of introducing in many cases, in one way or another, definite corrections (for example, of the type of the generally known Sho-

**Table 2**

### Differences of interatomic distances in diatomic molecules of halides of the alkali elements

Element	F	$\Delta r_{\text{Cl,F}}$	Cl	$\Delta r_{\text{Br,Cl}}$	Br	$\Delta r_{\text{J,Br}}$	J	Average
Li		0.49		0.15		0.22		
$\Delta r_{\text{Na,Li}}$	0.31		0.34		0.33		0.32	0.33
Na		0.52		0.14		0.21		
$\Delta r_{\text{K,Na}}$	0.29		0.31		0.32		0.34	0.31
K		0.54		0.15		0.23		
$\Delta r_{\text{Rb,K}}$	0.12		0.12		0.12		0.13	0.12
Rb		0.54		0.16		0.23		
$\Delta r_{\text{Rb,Cs}}$	0.10		0.12		0.13		0.14	0.12
Cs		0.56		0.17		0.24		
Average		0.53		0.15		0.23		

maker–Stevenson (<sup>16</sup>). The merit of the regularity considered above for estimating interatomic distances in molecules for which experimental data are lacking consists in the fact that the linear dependence of interatomic distances in series of similar molecules is realized regardless of whether it is possible to introduce a system of constant effective atomic radii such that the interatomic distance would be equal to their sum in the corresponding molecules. However, the possibilities for using the described comparative method are somewhat limited by the circumstance that, in order to estimate interatomic distances in some molecule, it is necessary to know the interatomic distances for all molecules of one series and the interatomic distances for two (and, in the particular case analyzed, one) members of the series to which the molecule under consideration belongs.

The regularity under discussion concerns interatomic distances in series of similar molecules. But this regularity may have broader significance if the concept of series of bonds of different types (or subtypes) is introduced, in which a linear change of interatomic distances is also observed.

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*Note: Figure translations are in progress. See original paper for figures.*

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