

GEOMETRY OF HALIDES OF ELEMENTS IN GROUP TWO OF THE PERIODIC SYSTEM

(UDC 539.193)

O. P. Charkin and M. E. Dyatkina

N. S. Kurnakov Institute of General and Inorganic Chemistry, Academy of Sciences, USSR
Translated from Zhurnal Strukturnoi Khimii, Vol. 5, No. 3,
pp. 451-454, May-June, 1964
Original article submitted January 19, 1964

The energies of valence states of the elements in group II of the periodic system are calculated. Based on the results, an attempt is made to consider qualitatively the geometry of alkaline-earth halides. It is shown that while the energy of the valence state in the sp configuration is 80-100 kcal less than for the corresponding states of all other configurations in the case of Be, Mg, Zn, Cd, and Hg, the energies of valence states in the sp and sd configurations lie close together in the case of Ca, Sr, Ba, and Ra. Hence, Ca, Sr, Ba, and Ra halides may be expected to have a nonlinear structure, contrary to Be, Mg, Zn, Cd, and Hg halides.

Until now it was widely believed that the halides of all elements in group II of the periodic system had molecules with a linear structure in the vapor phase (symmetry $D_{\infty h}$). In 1957, Akishin and Spiridonov, et al. [1] investigated the structure of about 30 MX_2 -type gaseous molecules (M is a group II element; $X = F, Cl, Br, \text{ or } I$) by electron diffraction. Values of $X-M-X$ angles found by them for Ca, Sr, and Ba compounds are given in Table 1. Akishin et al. [1] concluded from these data that all the indicated molecules were linear.

On considering the data given in Table 1, however, one notices that, firstly, the error in determining the angle is quite large, and secondly, the error increases in the order $Ca < Sr < Ba$ and decreases in the order $F > Cl > Br > I$. The error for fluorides is not stated, but in all probability it is even larger than for chlorides, since fluorine has less scattering power for electrons than the other halogens. Hence, the inference as to the linearity of CaF_2 , SrF_2 , BaF_2 , $CaCl_2$, $SrCl_2$, $BaCl_2$, $BaBr_2$, and BaI_2 molecules, for which the error exceeds $\pm 20^\circ$, cannot be considered conclusive.

Quite recently a paper by Wharton, Berg, and Klemperer [2] appeared in which an attempt was made to establish the presence or absence of a permanent dipole moment in Ca, Sr, and Ba halides. For this purpose, the behavior of molecular beams of halides in a nonuniform electric field was investigated. Under these conditions molecules which have only an induced dipole or whose permanent dipole μ is oriented along the field gradient are drawn into the field and do not affect the results of the measurements. Molecules having a permanent dipole moment oriented against the gradient are ejected by the field and focused on the detector aperture. Since the interaction energy of the dipole with the nonuniform electric field is proportional to μ , the voltage V_0 required to focus some given fraction of the molecular beam (e.g., 1%) may be used as a criterion of the dipole moment μ and hence, the angle $X-M-X$: the less V_0 is, the smaller is the angle $X-M-X$ and the larger is μ . Wharton, Berg, and Klemperer concluded that the BaF_2 , $BaCl_2$, $BaBr_2$, BaI_2 , SrF_2 , $SrCl_2$, and CaF_2 molecules each had a permanent dipole moment different from zero and hence, were nonlinear. The angle $X-M-X$ is about the same for BaF_2 , $BaCl_2$, and SrF_2 and slightly larger for $BaBr_2$, BaI_2 , $SrCl_2$, and CaF_2 . The permanent dipole moment decreases in the same order. The angle $X-M-X$ for BaF_2 , $BaCl_2$, and SrF_2 was estimated at approximately 120° . In the $SrBr_2$, SrI_2 , $CaCl_2$, and CaI_2 molecules $\mu = 0$, i.e., they are linear.

TABLE 1

	F	Cl	Br	I
Ca	180°	$180^\circ \pm 30^\circ$	$180^\circ \pm 10^\circ$	$180^\circ \pm 10^\circ$
Sr	180°	$180^\circ \pm 30^\circ$	$180^\circ \pm 10^\circ$	$180^\circ \pm 10^\circ$
Ba	180°	$180^\circ \pm 40^\circ$	$180^\circ \pm 30^\circ$	$180^\circ \pm 20^\circ$

As is evident, the conclusions reached in [1] and [2] do not agree. In this case, however, it should be noted that the data of Table 1 do not contradict the conclusions of Wharton et al. owing to the large error in determining the angle $X-M-X$.

TABLE 2. Slater-Condon Parameters of Elements in Group II of the Periodic System

Element	sp		sd		p ²		p,d			d ²		
	F ₀ (sp)	G ₁ (sp)	F ₀ (sd)	G ₂ (sd)	F ₀ (pp)	F ₂ (pp)	F ₀ (pd)	F ₂ (pd)	G ₁ (pd)	G ₂ (pd)	F ₀ (dd)	F ₂ (dd)
Be	32 273 *	10292 *	63 241	1187	60 830 *	857 *	95 000
Mg	28 471 *	6658 *	47 150	-750	55 509 *	1036 *	37 840 *
Ca	19 458 *	4195 *	21 103 *	740 *	40 097 *	93 *	8 *	427 †	18 †
Zn	39 701	7024	62 610	-150	80 719	76
Sr	18 150	3550	19 200	975	36 346	102	-10 †
Cd	37 340	6350	59 360	-140	368 †
Ba	15 580	2450	10 400	1000	25 320	24	2
Hg	47 940	6130	71 360	-40
Ra	18 055	2657	15 960	1390	31 080	120

* Data taken from [3].

† Data taken from [4].

The purpose of the present study was to attempt to consider qualitatively the geometry of MX_2 molecules, based on the energies of valence states of the metal atoms. For this we calculated the energies of valence states (EVS) of group II elements for the low-lying sp, sd, p², d², and pd configurations. (In determining EVS one must take account of the energy required to raise the atom from the ground state to the "valence" state in which it occurs in the molecule. The Slater-Condon parameters (Table 2) required for calculating EVS were taken from [3] and [4] for some of the elements; for the rest they were calculated by the method of least squares from Slater's equations [5] (spin-orbit coupling and configuration interaction were not taken into account) and experimental data on atomic spectra, tabulated by Moore [6]. The formulas for the valence states were taken from [7] and [4]. The results of the EVS calculations are given in Table 3. For convenience, curves of change of EVS over the group are shown in the figure, the data for subgroups IIA and IIB being separated in view of the marked difference in character of the corresponding curves.

Since the EVS are a characteristic of the central atom only, calculation of the specific properties of substituents X remains outside our consideration. Even with such a rough approach, however, the following conclusions can be drawn:

1. Of the five configurations sp, sd, p², d², and pd considered for all group II elements, the lowest and hence, energetically most favorable are the sp and sd configurations. Excitation to valence states of the other configurations requires 50-80 kcal more energy than such excitation in the sp and sd ones. Hence, it may be considered that only sp and sd electrons can take part in chemical bond formation in MX_2 molecules. Linear ($X-M-X=180^\circ$) MX_2 molecules result from sp hybridization and nonlinear ($X-M-X=90^\circ$) ones from sd hybridization, the latter being more favorable, from the viewpoint of Pauling's "bond strength" criterion, for the formation of two chemical bonds, since the angular parts of the hybrid orbitals have the maximum values 4.152 and 3.864 for the sd and sp configurations, respectively [8].

2. On comparing the EVS of the sp and sd configurations [$E_{VS}(sp)$ and $E_{VS}(sd)$], the group II elements may be divided clearly, according to the ratio of these energies, into two subgroups (which should not be confused with subgroups IIA and IIB). The first comprises Be, Mg, Zn, Cd, and Hg, and the second, Ca, Sr, Ba, and Ra. For elements of the first subgroup, $E_{VS}(sd)$ is 70-100 kcal higher than $E_{VS}(sp)$. In these elements, therefore, chemical bonds are formed by sp electrons only, so that MX_2 molecules are linear. This conclusion agrees fully with experimental data.

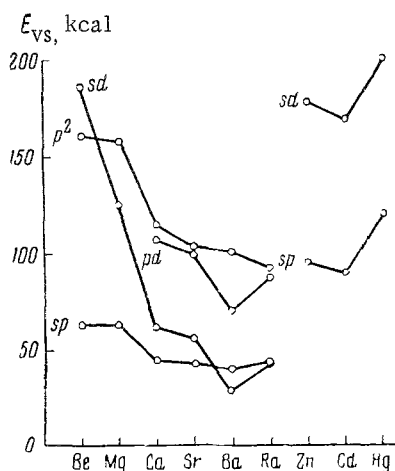
For Ca, Sr, Ba, and Ra the corresponding values of $E_{VS}(sp)$ and $E_{VS}(sd)$ lie close together, and hence, both these configurations can take part to about the same degree in chemical bond formation. Hence, it may be expected that MX_2 molecules of these elements will be nonlinear; the $X-M-X$ angle will vary from 90 to 180°, depending on how much the sd configuration contributes to the chemical bond.

3. It follows from Table 3 that in Ca and Sr the $E_{VS}(sd)$ are

TABLE 3. Energies of Valence States of Elements in Group II of the Periodic System (in kcal)

Configuration	Symmetry	S_h	Be	Mg	Ca	Zn	Sr	Cd	Ba	Hg	Ra
sp	$D_{\infty h}$	3,864	63	63	44	94	42	89	39	120	42
sd	C_{2v}	4,152	~186	~135	61	179	55	169	28	202	42
p^2	C_{2v}	3,464	~161	~158	~115	~220	~103	~208	~100	—	—
pd	$D_{\infty h}$	5,612	~280	~230	~108	~230	~100	~218	~95	—	~90
d^2	C_{2v}	4,418	—	—	~138	—	~126	—	~100	—	—

* S_h is "bond strength" according to Pauling [8].



respectively 17 and 13 kcal higher than the $E_{vs}(sp)$, in Ra both valence states have the same excitation energy, and in Ba $E_{vs}(sd)$ lies 11 kcal below $E_{vs}(sp)$. On the approximate assumption that the relative degree of participation of a given valence state in the chemical bond increases with decreasing excitation energy, one may expect that for a given X the degree of participation of the sd configuration in chemical bond formation will increase in the order $Ca < Sr < Ra < Ba$. The value of μ increases and the angle $X-M-X$ decreases in the same order. Since $E_{vs}(sd) \approx E_{vs}(sp)$ for Ra, $\angle X-Ra-X$ may be estimated at approximately 135° ; $\angle X-Ba-X$ is slightly smaller ($120-125^\circ$), whereas $\angle X-Ca-X$ and $\angle X-Sr-X$ are slightly larger ($140-150^\circ$).

4. As stated above, the specific properties of the substituents X were not taken into account in determining the energy of the valence state. From Table 3, however, it is evident that since the $E_{vs}(sd)$ in Ca and Sr are respectively 17 and 13 kcal higher than the $E_{vs}(sp)$, use of the sd configuration can be favorable only for ligands giving strong M-X bonds (i.e., F and Cl), and not for ligands forming weaker M-X bonds (Br and I). It follows from the data of Wharton et al. that the permanent dipole moment in Ca and Sr

compounds is different from zero only in the case of SrF_2 , $SrCl_2$, and CaF_2 . In the other cases ($SrBr_2$ and SrI_2 , $CaCl_2$ and $CaBr_2$) use of the sd configuration is unfavorable, and the corresponding molecules are linear.

In Ra halides both configurations take part to the same degree in bonds regardless of the type of ligand, since $E_{vs}(sd) = E_{vs}(sp)$ for Ra. Presumably the angle $X-M-X$ will not vary substantially as X changes.

In the case of Ba also, one should expect the $X-Ba-X$ angle to be nearly independent of the type of substituent. The increase in V_0 , found by Wharton et al. for BaI_2 , is probably explained by steric interaction of the I nuclei.

LITERATURE CITED

1. P. A. Akishin and V. P. Spiridonov, *Kristallografiya* **2**, 475 (1957); P. A. Akishin, V. P. Spiridonov, G. A. Sobolev, and V. A. Naumov, *Zh. fiz. khimii* **31**, 461, 648, 1871 (1957); **32**, 58 (1958).
2. L. Wharton, R. A. Berg, and W. Klemperer, *J. Chem. Phys.* **39**, 2023 (1963).
3. J. Hinze and H. H. Jaffe, *J. Chem. Phys.* **38**, 1834 (1963).
4. H. A. Skinner, *Trans. Faraday Soc.* **51**, 1036 (1955).
5. E. Condon and G. Shortley, *Theory of Atomic Spectra* [Russian translation], Moscow, IL (1949), Chapters VI and VII.
6. C. Moore, *Atomic Energy Levels*. Nat. Bur. Stand. V. **1**, (1949), **2** (1952), **3** (1958).
7. G. Pilcher and H. A. Skinner, *J. Inorg. Nucl. Chem.* **24**, 937 (1962).
8. M. G. Shirmazan, Candidate's dissertation, Moscow, L. Ya. Karpov Inst. Phys. Chem. (1950).