International Journal of Scientific and Technological Research
ISSN 2422-8702 (Online), **DOI:** 10.7176/JSTR/5-8-10
Vol.5, No.8, 2019

Molecular Structure of Monomeric Cadmium-Dihalides, $CdCl_2$, $CdBr_2$, CdF_2, CdI_2

Mustafa Caliskan
Trakya University Faculty of Science, Department of Physics, Edirne, Turkey
E-mail: caliskanmustafa@yahoo.com

Abstract

The geometrical parameters, namely, bond lengths and bond angles of cadmium dihalides were calculated from different levels of computation and experimentally. Several ab initio studies have been carried out. Most of them were assuming linearity for $CdCl_2$. On the other hand, computational studies show that the monomeric cadmium dihalides were assigned linear geometries [1, 2].

In this work we have calculated the equilibrium structure of the Cadmium dihalides using the interionic force model. The computed bond lengths and bond angles are in a good agreement with measured values from electron diffraction (ED) and quantum chemical calculations such as, LDF and QCISD. Supposing linearity of the molecules their ν_3 bending frequencies were estimated from electron diffraction, except cadmium diiodide molecule that was fitted to ν_1 mode frequency. We have made use of the simplifying features that have previously been established in similar studies of other ionic compounds which are the transferability of parameters describing the halogen ion [3, 4, 5].

It has been shown that the interionic force model is capable of the molecular structures of cadmium dihalides.

Keywords: Cadmium Dihalides, Interionic Force Model, chloride, fluoride, bromide, iodide

DOI: 10.7176/JSTR/5-8-10

1. Introduction

In molecular structure determination, experimental and computational techniques have been used in a concerted way there by enhancing each other's potentials. A first of a few examples can be found to demonstrate the combination of experiment and computation in the study of metal halides concerns alkaline earth dihalides. The two bridge structure had been generally accepted for the alkaline dihalides and without the computations the three bridge structure might have never been discovered [1]. This is a well known effect in structural chemistry. The effect involves the coupling the electronic and vibrational motions of the molecule [1,2]. Supposing that $CdCl_2$ has a planar linear symmetry structure as other transition metal dihalides. Recently, Hargittai and co-workers [1] have been reported the electron diffraction investigation of cadmium dihalides together with quantum chemical calculations based on the experimental vibrational spectrum data [1,2].

In this work, we present an theoretical calculations based on the interionic force model which is successfully used described the inter-ionic interactions in molten salts previously [3,4,5]. We evaluate an ionic model for the potential energy function of cadmium dihalides. Then we find stable structure. The results are tested by obtaining the molecular shapes for the CdX_2 monomers which the spectral data are available from the work of Hargittai et al [1]. Based on the interionic force model, we describe the pair interactions in a CdX_2 molecule at equilibrium structure.

2. Theory

2.1 Interionic Force Model

Following the earlier studies of the aluminium, rare-earth fluorides [4,5] and Al and Ga based halides [3], we use the interionic force model for manganese fluoride clusters incorporates

(i) the Born model of cohesion in the crystalline state which attributes binding to elecrostatic interactions between ions and describes the equilibrium state, *(ii)* the shell model for vibrational motions and crystal defects. Electron-shell deformability is described through effective valences Z_i and the electric and overlap polarizabilities of the halogens (denoted by α_X and α_S, respectively) and the electric polarizability α_M

of the Cadmium ions. Overlap repulsions of exponential form involve ionic radii R_i and stiffness parameters ρ_i. Van der Waals dipole-dipole interactions are included for halogens. We write the potential energy $U(\{r_{ij}\},\{p_i\})$ of a cluster, as a function of the interionic bonds r_{ij} and of the electric dipole moments p_i carried by the ions, as

$$U(\{r_{ij}\},\{p_i\}) = \sum_{i>j} V_{ij}(r_{ij}) + U_{pol}^{cl} + \frac{\alpha_s}{\alpha_{cl}} \sum_{i_m, j_h} p_j \,.\, \hat{r}_{ij} \left| \frac{d\Phi_{ij}(r_{ij})}{dr_{ij}} \right| \tag{1}$$

where $V_{ij}(r_{ij})$ is defined as

$$V_{ij}(r_{ij}) = \frac{Z_i Z_j e^2}{r_{ij}} + \phi_{ij}(r_{ij}) - \frac{C_i C_j}{r_{ij}^{\,6}} \,. \tag{2}$$

In the above equation the central potential $\phi_{ij}(r_{ij})$ described the overlap repulsive energy can be written in the form proposed by Busing [12].

$$\Phi_{ij}(r_{ij}) = f(\rho_i + \rho_j) \exp\left[\frac{R_i + R_j - r_{ij}}{\rho_i + \rho_j}\right] \tag{3}$$

where $f = 0.05\, e^2 / Å^2$ is a constant fixing the energy scale. The form (3) assumes that each ion has transferable interaction strengths, thus reducing the number of parameters which are needed for each family of compounds. For more details about the Interionic Force model for ionic clusters the reader is referred to Ref.[3,4]. However in this work we present a refined classical model of ionic interactions in $CdCl_2$ molecular ion.

3. Results and Discussion

Firstly, we present the equilibrium structure of cadmium dihalides obtained from the interionic force model. The equilibrium structure of CdX_2 molecule is described as follows :

The potential energy function of a molecule is computed by taking into account two functions, namely *(i)* one is for the optimization of a given configuration of the molecule by minimization of its energy towards states of static (stable and unstable) equilibrium and *(ii)* second one is for the evaluation of its vibrational frequencies and of its dynamical evalution at constant energy.

The parameters which enter the short-range overlap interactions involving Cl ion can be taken from earlier studies of alkali halides [3,4,5], while a simple proportionality holds between R_i and ρ_i for the metal ions ($R_M / \rho_M = 18.6$). With the above simplifications our model for Cd chloride involves three disposable parameters. These are *(i)* the ionic radius of the Cd ion R_M *(ii)* the effective valance of the Cd ion Z_M; and *(iii)* the electrical polarizability of the chloride ion α_X. We take $C_X = 5.5$ e$Å^{5/2}$, $\alpha_s = 0.49 Å^3$ [3,4]. The model parameters used in our calculations reported in Table 1.

Table 1. Interionic force parameters in Cd - chlorides, bromides, fluorides, iodides (the subscrips M and X denote the divalent-metal ion and the halogen ion) .

	Z_M	Z_X	R_M(Å)	ρ_M(Å)	R_X(Å)	ρ_X(Å)	C_X ($eÅ^{5/2}$)	α_X	α_s
$CdCl_2$	1.52	-0.76	1.12	0.0615	1.71	0.238	5.5	2	0.49
$CdBr_2$	1.46	-0.73	1.12	0.0602	1.84	0.258	7.17	3.05	0.76
CdF_2	1.2	-0.6	1.12	0.0602	1.32	0.215	2.08	0.88	0.2
CdI_2	1.424	-0.712	1.12	0.0602	2.02	0.289	10.1	6.29	1.7

We report our results for the geometrical structure of the $CdCl_2$ monomer for the linear symmetries in Table 2, respectively. Our results for the shape of this molecule can be compared with those obtained from electron diffraction (ED) and with the results of quantum chemical calculations such as, LDF reported in the review of Hargittai [1]. Table 2 reports our results for equilibrium bond lengths and bond angles with linear symmetry comparing with the results of ED.

Table 2. Geometrical parameters of monomerics $CdCl_2$, CdBr2, CdF2, CdI2 .Distances are in Å .

MX_2	Bond length (Å)	Present work	ED	LDF	QCISD
$CdCl_2$	r ($Cd\text{-}Cl_1$)	2.276	2.284 [a]	2.28 [b]	-
	r ($Cd\text{-}Cl_2$)	2.276	-	-	-
	r ($Cl_1 \cdots Cl_2$)	4.551	-	-	-
$CdBr_2$	r ($Cd\text{-}Br_1$)	2.394	2.394 [c]	2.41[d]	-
	r ($Cd\text{-}Br_2$)	2.394	-	-	-
	r ($Br_1 \cdots Br_2$)	4.782	-	-	-
CdF_2	r ($Cd\text{-}F_1$)	1.925	-	1.93 [e]	1.920 [f]
	r ($Cd\text{-}F_2$)	1.925	-	-	-
	r ($F_1 \cdots F_2$)	3.851	-	-	-
CdI_2	r ($Cd\text{-}I_1$)	2.589	2.582 [g]	2.60 [h]	-
	r ($Cd\text{-}I_2$)	2.589	-	-	-
	r ($I_1 \cdots I_2$)	5.156	-	-	-

Bond Lengths of Group 12 Dihalides from Experiment Computation.
[a]Ref [7,8],[b]Ref [9],[c]Ref [10,11], [d]Ref [9],[e]Ref [9],[f]Ref [12],[g]Ref [13],[h]Ref [9].

It appears that the calculated bond lengths using the interionic force model give a rather good agreement with ED. As the bond angles, we have $Cl_1\text{-}Cd\text{-}Cl_2$ bond angles some what smaller than those obtained by ED. Figure 1 shows the possible linear symmetry arrangement of $CdCl_2$. $\angle Cl_1\text{-}Cd\text{-}Cl_2 = 179.19$ degree.

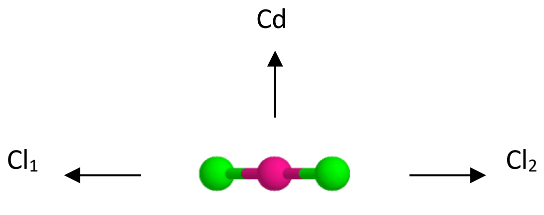

Figure 1. The expected cadmium dichloride molecule with linear symmetry.

We note that the interionic force model parameters are also the fitted the vibrational frequencies for the ground state molecules of $CdCl_2$ which the values taken from M. Hargittai [1]. Frequencies are taken as 427 cm^{-1} both for $CdCl_2$ in gas-IR assignments.

It appears that the calculated bond lengths using the interionic force model give a rather good agreement with ED. As the bond angles, we have Br_1-Cd-Br_2 bond angles some what smaller than those obtained by ED. Figure 2 shows the possible linear arrangement of $CdBr_2$.

$\angle Br_1$-Cd-Br_2 = 174.79 degree.

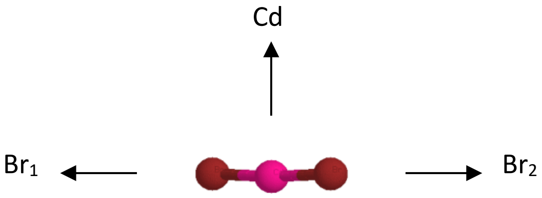

Figure 2. The expected cadmium dibromide molecule with linear symmetry.

We note that the interionic force model parameters are also the fitted the vibrational frequencies for the ground state molecules of $CdBr_2$ which the values taken from M. Hargittai [1]. Frequencies are taken as 315 cm^{-1} both for $CdBr_2$ in gas-IR assignments.

We report our results for the geometrical structure of the CdF_2 monomer for the linear symmetries in Table 2, respectively. Our results for the shape of this molecule can be compared with those obtained from the results of quantum chemical calculations such as, LDF and QCISD reported in the review of Hargittai [1].

It appears that the calculated bond lengths using the interionic force model give a rather good agreement. As the bond angles, we have F_1-Cd-F_2 bond angles. Figure 3 shows the possible linear symmetry arrangement of CdF_2 . $\angle F_1$-Cd-F_2 = 179.76 degree.

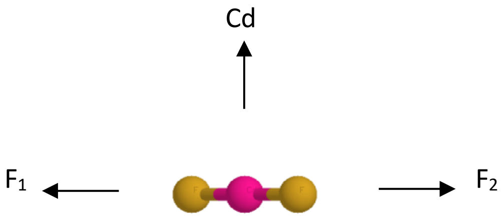

Figure 3. *The expected cadmium difluoride molecule with linear symmetry.*

We note that the interionic force model parameters are also the fitted the vibrational frequencies for the ground state molecules of CdF_2 which the values taken from M. Hargittai [1]. Frequencies are taken as 543 cm^{-1} both for CdF_2 in est.gas-phase assignments.

We report our results for the geometrical structure of the CdI_2 monomer for the linear symmetries in Table 2, respectively. Our results for the shape of this molecule can be compared with those obtained from electron diffraction (ED) and with the results of quantum chemical calculations such as LDF reported in the review of Hargittai [1]. Table 2 reports our results for equilibrium bond lengths and bond angles with linear symmetry comparing with the results of ED.

It appears that the calculated bond lengths using the interionic force model give a rather good agreement with ED. As the bond angles, we have I_1-Cd-I_2 bond angles some what smaller than those obtained by ED. Figure 4 shows the possible linear symmetry arrangement of CdI_2 .

$\angle I_1$-Cd-I_2 = 169.69 degree.

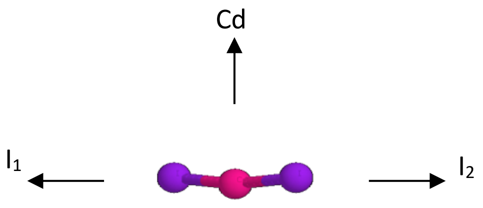

Figure 4. *The expected cadmium diiodide molecule with linear symmetry.*

We note that the interionic force model parameters are also the fitted the vibrational frequencies for the ground state molecules of CdI_2 which the values taken from M. Hargittai [1]. Frequencies are taken as 265 cm^{-1} both for CdI_2 in gas-IR assignments.

It has been reported that the electron diffraction experiments in conjunction with vibrational spectroscopic data give the best agreement for a linear model for $CdCl_2$, but a quasilinear model with a bond angle of about 165-180^0 and a low potential barrier could not be ruled out.

Table 3. Interionic Force Model and Gas – Phase Vibrational Frequencies (in cm^{-1}) of Group 12 Metal Dihalides from Experiment.

		ν_1	Ref	ν_2	Ref	ν_3	Ref
$CdCl_2$	Present work	331		50		427.22	
	Experiment	337	1	72	8	427	14
$CdBr_2$	Present work	203		37		315.26	
	Experiment	209	16	57	11	315	14
CdF_2	Present work	439		60		493	
	Experiment	543	1	121	17	661.7	17
CdI_2	Present work	146		34		265.79	
	Experiment	153	18	50	15,19,20	265	14,15

4. Conclusions

In this work, we present a simple ionic force model for the cadmium dihalides. Our results give a useful first estimation of an ionic model for CdX_2 .

References

[1] M. Hargittai, Chem. Rev. **100**, 2233 (2000).

[2] M. Hargittai, Coord. Chem. Rev. **91**, 35 (1988).

[3] Z. Akdeniz, M. Çaliskan, Z. Çiçek, M. P. Tosi, Z. Naturforsch. **55a**, 575 (2000).

[4] Z. Akdeniz, Z. Çiçek, M. P. Tosi, Z. Naturforsch. **55a**, 861 (2000).

[5] Z. Akdeniz, A. Karaman, M. P. Tosi, Z. Naturforsch. **56a**, 376 (2001).

[6] M. Kaupp, H. G. von Schnering, Inorg. Chem. **33**, 4718 (1994).

[7] A. Haaland, K.-G. Martinsen, J. Tremmel, J. Acta Chem. Scand. **46**, 589 (1992).

[8] N. Vogt, A. Haaland, K.-G. Martinsen, J. Vogt, J. Acta Chem. Scand. **47**, 937 (1993).

[9] M. S. Liao, Q. E. Zhang, Inorg. Chem. **34**, 5597 (1995).

[10] V. M. Petrov, A.N. Utkin, G.V. Girichev, A.A. Ivanov, Russ. J. Struct. Chem. **26**, 189 (1985).

[11] A. G. Gershikov, Russ. J. Struct. Chem. **30**, 841 (1989).

[12] M. Kaupp, M. Dolg, H. Stoll, H. G. von Schnering, Inorg. Chem. **33**, 2122 (1994).

[13] N. Vogt, M. Hargittai, M. Kolonits, I. Hargittai, Chem. Phys. Lett. **199**, 441 (1992).

[14] W. Klemperer, J. Chem. Phys. **25**, 1066 (1956).

[15] R. J. M. Konings, A. S. Booij, E. H. P. Cordfunke, Vib. Spectrosc. **2**, 251 (1991).

[16] A. Strull, A. Givan, A. Loewenschuss, J. Mol. Spectrosc. **62**, 283 (1976).

[17] A. Givan, A. Loewenschuss, J. Chem. Phys. **72**, 3809 (1980).

[18] I. R. Beattie, P. J. Jones, B. R. Bowsher, T. R. Gilson, Vib. Spectrosc. **4**, 373 (1993).

[19] G.K. Selivanov, N.I. Zavalishin, A.A. Maltsev, Vest. Mosk. Univ. Ser. Khim. **28**, 712 (1972).

[20] A.A. Maltsev, G.K. Selivanov, V.J. Yampolski, N.I. Zavalishin, Nat. Phys. Sci. **231**, 158 (1971).