

# Theoretical Study of Structure and Vibrational Spectra of Molecular and Ionic Clusters Existing in Vapour over Rubidium Chloride

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## To cite this article:

Ismail Abubakari, Tatiana Pogrebnaya, Alexander Pogrebnoi. Theoretical Study of Structure and Vibrational Spectra of Molecular and Ionic Clusters Existing in Vapour over Rubidium Chloride. *American Journal of Applied Chemistry*. Vol. 3, No. 6, 2015, pp. 224-231.

doi: 10.11648/j.ajac.20150306.18

**Abstract:** The geometrical structure and the vibrational spectra of dimer  $\text{Rb}_2\text{Cl}_2$ , trimer  $\text{Rb}_3\text{Cl}_3$ , tetramer  $\text{Rb}_4\text{Cl}_4$  molecules and heptaatomic  $\text{Rb}_4\text{Cl}_3^+$ ,  $\text{Rb}_3\text{Cl}_4^-$  ions were studied. The cluster molecules and ions had been detected in equilibrium vapour over rubidium chloride previously. The quantum chemical calculations by DFT with hybrid functional B3P86 and MP2 methods were performed. The effective core potential with Def2-TZVP (6s4p3d) basis set for rubidium atom and full electron aug-cc-pVTZ (6s5p3d2f) basis set for chlorine atom were used. The equilibrium configuration was confirmed to be rhomb of symmetry  $D_{2h}$  for dimer  $\text{Rb}_2\text{Cl}_2$ , distorted cube ( $T_d$ ) for tetramer  $\text{Rb}_4\text{Cl}_4$  and polyhedral ( $C_{3v}$ ) for heptaatomic ions  $\text{Rb}_4\text{Cl}_3^+$  and  $\text{Rb}_3\text{Cl}_4^-$ . For the trimer molecule  $\text{Rb}_3\text{Cl}_3$  two isomers have been revealed: hexagonal ( $D_{3h}$ ) and butterfly-shaped ( $C_{2v}$ ), the latter has lower energy and is proved to be predominant in equilibrium vapour in a broad temperature range.

**Keywords:** Ionic and Molecular Clusters, Rubidium Chloride, Geometrical Structure, Vibrational Spectra, DFT, MP2, Isomers

## 1. Introduction

Several alkali metals including rubidium may chemically combine with halogen to form different neutral and ionic clusters which exist in vapours [1–10]. These clusters are characterized by different geometrical structures, vibrational spectra, and thermodynamic properties which are mostly depend on the number of atoms composing the species [1]. The formed clusters possess specific electronic, optical, magnetic and structural properties which make them useful in different technical and scientific applications [2, 3]. These properties are also strongly depending on size and composition of the clusters. Changing the magnitude and structure of a cluster aggregate allows coming up with new materials of desired properties [11].

To investigate the structure and properties of alkali halide clusters, different experimental techniques e.g. high temperature mass spectrometry [12, 13], microwave absorption spectroscopy [14, 15] and molecular beam electric

resonance [16] and theoretical methods [1, 17–21] were employed.

Different molecular and ionic associates were detected in vapour over rubidium chloride; they are dimer, trimer, and tetramer molecules and the ions  $\text{Rb}^+(\text{RbCl})_n$  ( $n = 1-4$ ) [22].

Previously the quantum chemical methods has been used to study tri- and pentaatomic ions  $\text{Rb}_2\text{Cl}^+$ ,  $\text{RbCl}_2^-$ ,  $\text{Rb}_3\text{Cl}_2^+$ ,  $\text{Rb}_2\text{Cl}_3^-$  [20]. The ionic clusters were studied by density functional theory (DFT) with the Becke–Lee–Yang–Parr functional (B3LYP5), second order and fourth order Møller–Plesset perturbation theory (MP2 and MP4) using the basis sets aug-cc-pVTZ (5s4p2d1f) for Cl and cc-pVTZ (7s5p4d1f) for Rb [20]. This study aims the investigation of the structure and properties of neutral and heavier ionic clusters of rubidium chloride.

## 2. Methodology

The density functional theory (DFT) with hybrid functional the Becke–Perdew correlation B3P86 [23–26] and second

order Møller–Plesset perturbation theory (MP2) implemented into PC GAMESS (General Atomic and Molecular Electronic Structure System) program [27] and Firefly version 8.1.0 [28] were used for calculation of geometrical parameters and frequencies of normal vibrations. The visualization of the geometrical structure, specification of parameters, and assignment of vibrational modes in infrared spectra was done using the Chemcraft software [29] and MacMolPlt program [30]. The effective core potentials with Def2–TZVP (6s4p3d) basis set for Rb atom [31, 32] and full electron aug–cc–pVTZ basis set for Cl (6s5p3d2f) atom [32, 33] were applied in this study. The basis sets were taken from the EMSL (The Environmental Molecular Sciences Laboratory, GAMESS US) Basis Set Exchange version 1.2.2 library [34, 35].

The Openthermo software [36] was used in calculation of the thermodynamic properties including energies  $\Delta_r E$  and enthalpies  $\Delta_r H^\circ(0)$  of the reactions which were calculated through the following equations:

$$\Delta_r E = \sum E_{i \text{ prod}} - \sum E_{i \text{ reactant}} \quad (1)$$

$$\Delta_r H^\circ(0) = \Delta_r E + \Delta_r \epsilon \quad (2)$$

$$\Delta_r \epsilon = \frac{1}{2}hc(\sum \omega_{i \text{ prod}} - \sum \omega_{i \text{ reactant}}) \quad (3)$$

where  $\sum E_{i \text{ prod}}$ ,  $\sum E_{i \text{ reactant}}$  are the sums of the total energies of the products and reactants respectively,  $\Delta_r \epsilon$  is the zero point vibration energy correction,  $\sum \omega_{i \text{ prod}}$  and  $\sum \omega_{i \text{ reactant}}$  are the sums of the vibration frequencies of the products and reactants respectively.

### 3. Results and Discussion

#### 3.1. Monomer RbCl and dimer Rb<sub>2</sub>Cl<sub>2</sub>

The properties of the diatomic RbCl and dimer Rb<sub>2</sub>Cl<sub>2</sub> molecules was computed using three different DFT hybrid functionals, B3LYP5, B3P86 and B3PW91 and Møller–Plesset perturbation theory (MP2) for the purpose of choosing the appropriate method to be implemented in this study and estimation of uncertainties in theoretical values. The results for diatomic molecule RbCl together with the available experimental data are shown in Table 1.

**Table 1.** Properties of the monomer molecule RbCl.

Property	B3LYP5	B3P86	B3PW91	MP2	Ref data
$R_e(\text{Rb-Cl})$	2.878	2.857	2.860	2.855	2.787 [37]
$-E$	484.32782	484.42116	484.38973	483.40565	
$\omega_e$	219	222	221	228	228 [38] 233 [39]
$\mu_e$	11.0	10.9	10.9	11.4	10.483 [40]
$IE_{\text{vert}}$	8.45	8.66	8.53	8.52	$8.50 \pm 0.03$ [41] $8.3 \pm 0.1$ [42, 43]
$IE_{\text{ad}}$	8.17	8.38	8.25		
$EA$	0.58	0.67	0.60	0.49	$0.543 \pm 0.01$ [44]

Notes: Here and hereafter,  $R_e$  is the equilibrium internuclear distance (Å),  $E$  is the total electron energy (au),  $\omega_e$  is the fundamental frequency ( $\text{cm}^{-1}$ ),  $\mu_e$  is the dipole moment (D),  $IE_{\text{vert}}$  and  $IE_{\text{ad}}$  are the ionization energies, vertical and adiabatic, respectively (eV),  $EA$  is the electron affinity (eV).

As is seen the calculated internuclear distance ( $R_e$ ) using three DFT hybrid functionals were overrated by 0.07–0.09 Å when compared with the reference data and that of MP2 was overrated by 0.07 Å. Considering both DFT and MP2 methods, the results obtained show very little variation whereas DFT/B3P86 and MP2 give the best results regarding to the reference. The calculated values of frequency were underrated by 6–9  $\text{cm}^{-1}$  (2.7–3.9%) for DFT methods while MP2 result coincides with the experimental value [38]. The results for dipole moment ( $\mu_e$ ), show high deviation from reference data for the case of MP2, overrated by 0.88 D; and overrated by 0.41–0.47 D for the DFT methods.

The adiabatic ionization energy ( $IE_{\text{ad}}$ ) was obtained as the energy difference of the  $\text{RbCl}^+$  ion and neutral molecule where the internuclear separation  $R_e(\text{Rb-Cl})$  was optimized both for neutral and ionic species and vertical ionization energy ( $IE_{\text{vert}}$ ) was obtained as the energy difference of the  $\text{RbCl}^+$  ion and neutral molecule where the internuclear separation  $R_e(\text{Rb-Cl})$  was optimized in neutral molecule only and accepted the same for the ion. Electron affinities ( $EA$ ) were obtained by determining the energy difference between neutral molecule and negatively charged ion. The results obtained for  $IE$  and  $EA$

using both DFT and MP2 methods agree well with the reference. As the optimization procedure by MP2 was not implemented for the species with multiplicity more than 1 in the software [27, 28], the  $IE_{\text{ad}}$  by MP2 method was not calculated in this study.

For the dimer molecule  $\text{Rb}_2\text{Cl}_2$ , a planar cyclic structure of  $D_{2h}$  symmetry (Fig. 1a) was confirmed to be equilibrium, while linear one ( $C_{\infty v}$ ) was found to be a saddle point on the potential energy surface. The calculated properties; internuclear distance, valence angle, vibrational spectra and enthalpy of the dissociation reaction are presented in Table 2. As seen the calculated values of internuclear distance are overrated by 0.04–0.09 Å compared with literature data [45] and the values of enthalpy of dissociation reaction are in agreement with the reference data [22, 46].

The absence of low frequencies in the vibrational spectra of  $\text{Rb}_2\text{Cl}_2$  indicates the rigidity of the structure; the lowest frequency being about 50  $\text{cm}^{-1}$ .

In the IR spectrum, three vibrational modes  $\omega_4$ ,  $\omega_5$ , and  $\omega_6$  have nonzero intensities but due to overlapping of  $\omega_5$  and  $\omega_6$  only two peaks could be seen which are asymmetrical stretching 171  $\text{cm}^{-1}$  and wagging 52  $\text{cm}^{-1}$  (MP2).

Based on results for the RbCl and Rb<sub>2</sub>Cl<sub>2</sub> molecules, it is worth to mention that the data obtained by MP2 and DFT/B3P86 hybrid functional agree better with the available

literature data therefore these two methods were chosen for further computations of heavier molecular and ionic clusters.

**Table 2.** Properties of the dimer molecule, Rb<sub>2</sub>Cl<sub>2</sub>.

Property	B3LYP5	B3P86	B3PW91	MP2	Ref. data
$R_e(\text{Rb}-\text{Cl})$	3.081	3.053	3.062	3.032	2.989 [45] <sup>a</sup>
$\alpha_e(\text{Cl}-\text{Rb}-\text{Cl})$	87.7	87.9	87.8	88.6	89.5 [45] <sup>a</sup>
$-E$	968.71721	968.90454	968.84018	966.87305	
$\Delta_r E$	161.6	163.4	159.4	162.1	
$\Delta_r H^\circ$	159.9	161.6	157.8	160.1	164±11 [22] 172.4 [46]
$\omega_1 (A_g)$	158	163	161	172	
$\omega_2 (A_g)$	66	64	66	68	
$\omega_3 (B_{1g})$	135	138	135	153	
$\omega_4 (B_{1u})$	49	48	49	52	
$\omega_5 (B_{2u})$	155	158	155	171	
$\omega_6 (B_{3u})$	157	160	156	171	
$I_4$	0.94	0.94	0.94	0.97	
$I_5$	1.61	1.62	1.64	1.70	
$I_6$	1.69	1.69	1.70	1.65	

Notes: <sup>a</sup>The MP2 calculation. Here and hereafter,  $\alpha_e$  is the valence angle (deg).  $\Delta_r E$  and  $\Delta_r H^\circ(0)$  are the energy and enthalpy of the dissociation reaction  $\text{Rb}_2\text{Cl}_2 \rightleftharpoons 2\text{RbCl}$  (kJ mol<sup>-1</sup>),  $I_i$  are the infrared intensities (D<sup>2</sup>·amu<sup>-1</sup>·Å<sup>-2</sup>). The reducible vibration representation reduces to  $\Gamma = 2A_g + B_{1g} + B_{1u} + B_{2u} + B_{3u}$ .

### 3.2. Trimers Rb<sub>3</sub>Cl<sub>3</sub> and tetramer Rb<sub>4</sub>Cl<sub>4</sub>

For the trimer molecule Rb<sub>3</sub>Cl<sub>3</sub>, three possible geometrical configurations were considered; linear of  $D_{\infty h}$  symmetry, hexagonal of  $D_{3h}$  symmetry and butterfly-shaped of  $C_{2v}$

symmetry. The linear configuration was found to be unstable due to presence of imaginary frequencies but the rest two configurations, (Figs. 1b and 1c) were confirmed to be equilibrium. The results are shown in Table 3.

**Table 3.** Properties of trimer Rb<sub>3</sub>Cl<sub>3</sub> molecule, hexagonal ( $D_{3h}$ ) and butterfly-shaped ( $C_{2v}$ ).

Rb <sub>3</sub> Cl <sub>3</sub> ( $D_{3h}$ )			Rb <sub>3</sub> Cl <sub>3</sub> ( $C_{2v}$ )		
Property	B3P86	MP2	Property	B3P86	MP2
$R_e(\text{Rb}-\text{Cl})$	3.051	3.032	$R_{e1}(\text{Rb}_1-\text{Cl}_4)$	2.997	2.982
			$R_{e2}(\text{Rb}_3-\text{Cl}_5)$	3.132	3.105
			$R_{e3}(\text{Rb}_2-\text{Cl}_6)$	3.093	3.068
			$R_{e4}(\text{Rb}_3-\text{Cl}_6)$	3.386	3.295
$\alpha_e(\text{Rb}-\text{Cl}-\text{Rb})$	117.9	119.5	$\alpha_e(\text{Rb}_2-\text{Cl}_5-\text{Rb}_3)$	91.8	91.9
$\beta_e(\text{Cl}-\text{Rb}-\text{Cl})$	122.1	120.5	$\beta_e(\text{Cl}_4-\text{Rb}_1-\text{Cl}_6)$	95.4	93.9
$-E$	1453.37224	1451.29449	$-E$	1453.37325	1451.29818
			$-\Delta_r E_{\text{iso}}$	2.6	9.7
$\omega_1 (A'_1)$	176	191	$\omega_1 (A_1)$	177 (1.79)	185 (1.82)
$\omega_2 (A'_1)$	126	127	$\omega_2 (A_1)$	128 (0.02)	135 (0.03)
$\omega_3 (A'_1)$	58	84	$\omega_3 (A_1)$	90 (0.25)	102 (0.44)
$\omega_4 (E')$	181	193	$\omega_4 (A_1)$	73 (0.24)	85 (0.07)
$\omega_5 (E')$	134	142	$\omega_5 (A_1)$	55 (1.21)	57 (1.23)
$\omega_6 (E')$	21	23	$\omega_6 (A_1)$	50 (0.03)	51 (0.01)
$\omega_7 (A''_2)$	46	48	$\omega_7 (A_2)$	28 (0)	28 (0)
$\omega_8 (E'')$	23	24	$\omega_8 (B_1)$	8 (0.01)	13 (0.02)
$I_4$	3.94	3.98	$\omega_9 (B_2)$	188 (1.25)	200 (1.38)
$I_5$	0.82	0.78	$\omega_{10} (B_2)$	172 (0.45)	181 (0.26)
$I_7$	1.40	1.45	$\omega_{11} (B_2)$	150 (1.03)	162 (1.08)
$I_8$	0.50	0.52	$\omega_{12} (B_2)$	53 (0.19)	53 (0.19)
			$\mu_e$	9.8	10.4

Notes:  $\Delta_r E_{\text{iso}} = E(C_{2v}) - E(D_{3h})$  is the relative energy of the butterfly-shaped isomer regarding the hexagonal one (kJ mol<sup>-1</sup>). The reducible vibration representations for Rb<sub>3</sub>F<sub>3</sub> of  $D_{3h}$  and  $C_{2v}$  symmetry reduces to  $\Gamma = 3A'_1 + 3E' + A''_2 + E''$  and  $\Gamma = 6A_1 + A_2 + B_1 + 4B_2$  respectively. For the  $C_{2v}$  butterfly-shaped isomer, the values given in parentheses near the frequencies are infrared intensities (D<sup>2</sup>·amu<sup>-1</sup>·Å<sup>-2</sup>).

For the hexagonal isomer ( $D_{3h}$ ), one internuclear distance  $R_e(\text{Rb}-\text{Cl})$  and one valence angle  $\alpha_e(\text{Rb}-\text{Cl}-\text{Rb})$  or  $\beta_e(\text{Cl}-\text{Rb}-\text{Cl})$  are needed to describe the structure; for the butterfly-shaped isomer ( $C_{2v}$ ), four internuclear distances  $R_{e1}$ ,  $R_{e2}$ ,  $R_{e3}$ ,  $R_{e4}$  and two valence angles  $\alpha_e(\text{Rb}_2-\text{Cl}_5-\text{Rb}_3)$  and

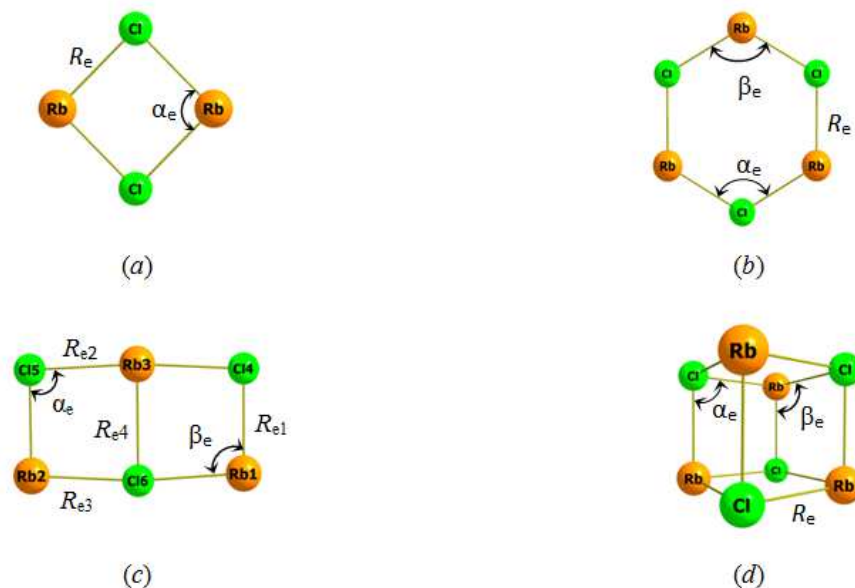
$\beta_e(\text{Cl}_4-\text{Rb}_1-\text{Cl}_6)$  are used for the description. The butterfly-shaped configuration has lower energy, by 2.6 kJ mol<sup>-1</sup> (DFT) and 10.0 kJ mol<sup>-1</sup> (MP2), than hexagonal one.

The relative concentration of isomers  $p(C_{2v})/p(D_{3h})$  have been estimated using the same procedure as it was described

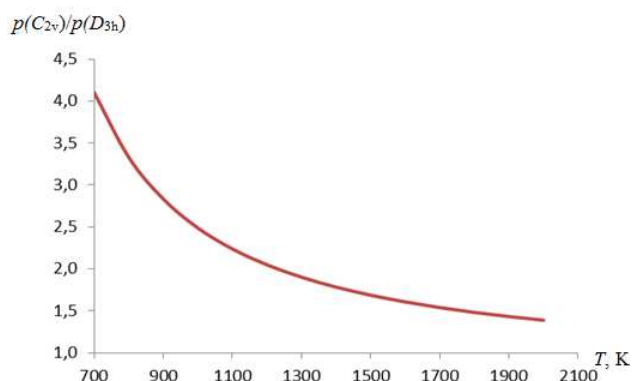
previously [21]. The enthalpy of the isomerization and relative energy of isomers  $\Delta_r E_{\text{iso}}$  (MP2) for the isomerization reaction  $\text{Rb}_3\text{Cl}_3 (D_{3h}) \rightleftharpoons \text{Rb}_3\text{Cl}_3 (C_{2v})$  was calculated using Eqs. (2) and (3).

The values of  $p(C_{2v})/p(D_{3h})$  were obtained for the

temperature range between 700–2000 K; the plot is shown in Fig. 2. As is seen the butterfly-shaped isomer is more abundant than hexagonal one and the concentration of the former decreases with temperature increase.



**Figure 1.** Equilibrium geometric structures of molecules: (a)  $\text{Rb}_2\text{Cl}_2 (D_{2h})$ ; (b)  $\text{Rb}_3\text{Cl}_3 (D_{3h})$ ; (c)  $\text{Rb}_3\text{Cl}_3 (C_{2v})$ ; (d)  $\text{Rb}_4\text{Cl}_4 (T_d)$ .

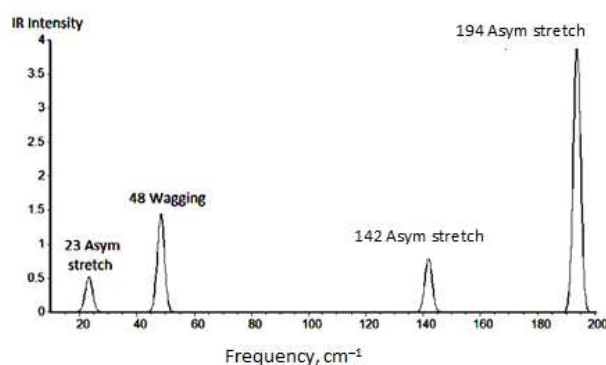


**Figure 2.** Temperature dependence of relative amount of the  $C_{2v}$  isomer regarding to  $D_{3h}$  isomer of trimer  $\text{Rb}_3\text{Cl}_3$  molecule.

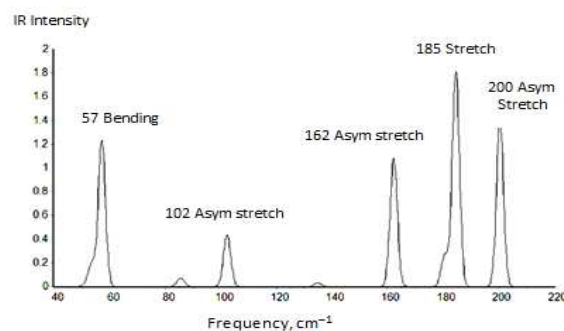
The IR spectra of both isomers of  $\text{Rb}_3\text{Cl}_3$  molecule are shown in Fig. 3. The most intensive bands correspond to the stretching vibration modes and bending modes have lower intensities.

When comparing the properties of  $\text{Rb}_3\text{Cl}_3$  with  $\text{Rb}_3\text{F}_3$  molecule, a similarity may be noted: the same two isomers were revealed for  $\text{Rb}_3\text{F}_3$  [21] and the butterfly-shaped isomer was predominant in that case as well.

For the tetramer molecule  $\text{Rb}_4\text{Cl}_4$ , the geometrical configuration considered was cube with  $T_d$  symmetry (Fig. 1d) and it was confirmed to be equilibrium. The geometrical parameters and vibrational frequencies of the tetramer molecule are presented in Table 4.



(a)



(b)

**Figure 3.** Theoretical IR spectra of the trimer  $\text{Rb}_3\text{Cl}_3$  molecule calculated by MP2 method: (a) hexagonal isomer ( $D_{3h}$ ); (b) butterfly-shaped isomer ( $C_{2v}$ ).

**Table 4.** Properties of tetramer molecule  $Rb_4Cl_4$ , cube of  $T_d$  symmetry.

Property	B3P86	MP2
$R_e(Rb-Cl)$	3.169	3.129
$\alpha_e(Rb-Cl-Rb)$	88.6	89.1
$\beta_e(Cl-Rb-Cl)$	91.4	90.9
$-E$	1937.87064	1935.11485
$\omega_1(A_1)$	138	145
$\omega_2(A_1)$	80	80
$\omega_3(E)$	119	128
$\omega_4(E)$	51	61
$\omega_5(T_1)$	116	127
$\omega_6(T_2)$	141	151
$\omega_7(T_2)$	137	146
$\omega_8(T_2)$	49	41
$I_6$	7.30	7.90
$I_7$	0.38	0.03
$I_8$	0.06	0.03

Notes: The reducible vibration representation reduces to  $\Gamma = 2A_1 + 2E + T_1 + 3T_2$

One internuclear distance  $R_e(Rb-Cl)$  and one valence angle  $\alpha_e(Rb-Cl-Rb)$  or  $\beta_e(Cl-Rb-Cl)$  are needed to describe the

structure. In the IR spectrum, three vibrational modes are active but only one peak could be observed  $\omega_6(T_2)$  which is assigned to asymmetrical stretching  $Rb-Cl$  vibration; other two modes have low intensities.

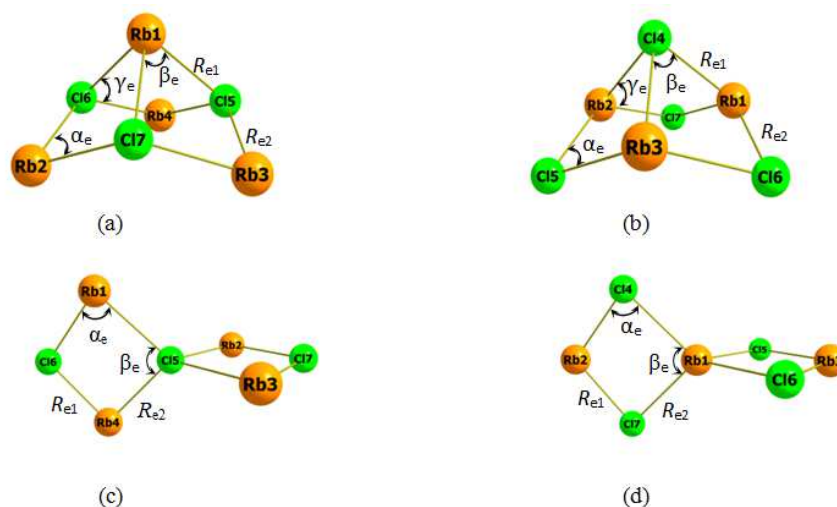
### 3.3. Heptaatomic Ions $Rb_4Cl_3^+$ and $Rb_3Cl_4^-$

For heptaatomic ions  $Rb_4Cl_3^+$  and  $Rb_3Cl_4^-$  two alternative structures were considered, polyhedral of  $C_{3v}$  symmetry and two-cycled with mutually perpendicular planes of  $D_{2d}$  symmetry (Fig. 4); only polyhedral structure of symmetry  $C_{3v}$  was confirmed to be equilibrium. The results for both positive and negative ions are presented in Table 5. The polyhedral structure is described by two internuclear distances  $R_{e1}$  and  $R_{e2}$  and three valence angles,  $\alpha_e(Rb_2-Cl_5-Rb_3)$ ,  $\beta_e(Rb_1-Cl_4-Rb_3)$  and  $\gamma_e(Cl_4-Rb_2-Cl_7)$ . Compared to the  $D_{2d}$  structure, the polyhedral configurations possesses lower energy with the energy drop of 87 kJ mol<sup>-1</sup> and 83 kJ mol<sup>-1</sup> for  $Rb_4Cl_3^+$  and  $Rb_3Cl_4^-$  respectively, according to MP2 results.

**Table 5.** Properties of the heptaatomic ions  $Rb_4Cl_3^+$  and  $Rb_3Cl_4^-$  ( $C_{3v}$ ).

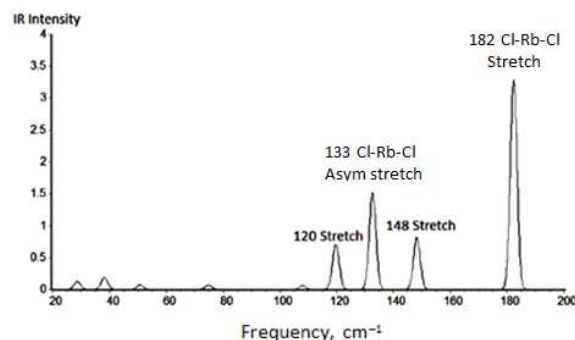
$Rb_4Cl_3^+$			$Rb_3Cl_4^-$		
Property	B3P86	MP2	Property	B3P86	MP2
$R_{e1}(Rb_1-Cl_5)$	3.191	3.150	$R_{e1}(Rb_1-Cl_4)$	3.198	3.154
$R_{e2}(Rb_3-Cl_5)$	3.117	3.089	$R_{e2}(Rb_1-Cl_6)$	3.147	3.116
$\alpha_e(Cl_6-Rb_2-Cl_7)$	87.8	86.6	$\alpha_e(Rb_2-Cl_5-Rb_3)$	84.7	85.1
$\beta_e(Cl_5-Rb_1-Cl_7)$	85.3	84.5	$\beta_e(Rb_1-Cl_4-Rb_3)$	83.0	83.8
$\gamma_e(Rb_1-Cl_6-Rb_4)$	89.2	89.9	$\gamma_e(Cl_4-Rb_2-Cl_7)$	91.2	90.9
$-E$	1477.41200	1475.10172	$-E$	1913.72426	1911.20087
$\omega_1(A_1)$	138 (0.61)	148 (0.82)	$\omega_1(A_1)$	138 (0.04)	146 (0.31)
$\omega_2(A_1)$	116 (0.91)	120 (0.71)	$\omega_2(A_1)$	134 (1.44)	141 (1.17)
$\omega_3(A_1)$	75 (0.06)	75 (0.07)	$\omega_3(A_1)$	72 (0.15)	74 (0.13)
$\omega_4(A_1)$	37 (0.15)	38 (0.19)	$\omega_4(A_1)$	50 (0.46)	51 (0.51)
$\omega_5(A_2)$	149 (0)	164 (0)	$\omega_5(A_2)$	126 (0)	138 (0)
$\omega_6(E)$	169 (3.28)	182 (3.30)	$\omega_6(E)$	147 (3.74)	157 (3.92)
$\omega_7(E)$	125 (1.56)	133 (1.52)	$\omega_7(E)$	132 (1.60)	140 (1.44)
$\omega_8(E)$	100 (0.02)	108 (0.06)	$\omega_8(E)$	108 (0.06)	120 (0.04)
$\omega_9(E)$	51 (0.08)	51 (0.08)	$\omega_9(E)$	54 (0.06)	54 (0.04)
$\omega_{10}(E)$	29 (0.10)	29 (0.12)	$\omega_{10}(E)$	31 (0.26)	31 (0.28)

Notes:  $\gamma_e$  is the valence angle (deg). The reducible vibration representations reduce to  $\Gamma = 4A_1 + A_2 + 5E$  for both  $Rb_4Cl_3^+$  and  $Rb_3Cl_4^-$

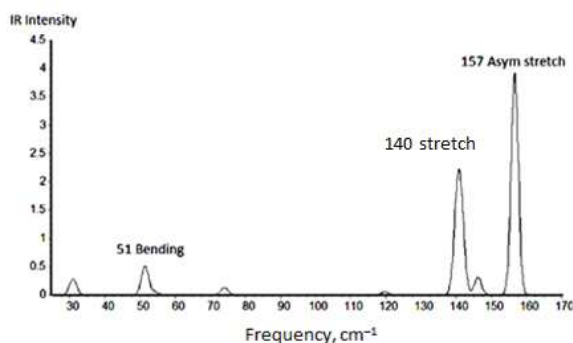


**Figure 4.** Geometric structures of heptaatomic ions: polyhedral of  $D_{3h}$  symmetry (a)  $Rb_4Cl_3^+$  (b)  $Rb_3Cl_4^-$ ; two cycled with the mutually perpendicular planes of  $D_{2d}$  symmetry (c)  $Rb_4Cl_3^+$  (d)  $Rb_3Cl_4^-$ .

As is seen in Table 5 the respective geometrical parameters and vibrational frequencies of the positive and negative ions are close to each other. The IR spectra are shown in Fig. 5. In both spectra, the stretching vibrational modes have higher intensities than bending modes.



(a)



(b)

**Figure 5.** Theoretical IR spectra of heptaatomic ions ( $C_{3v}$ ) calculated by MP2 method: (a)  $Rb_4Cl_3^+$ ; (b)  $Rb_3Cl_4^-$ .

## 4. Conclusion

The properties of the trimer and tetramer molecules and heptaatomic ionic clusters have been investigated theoretically using DFT/B3P86 and MP2 methods. The corresponding parameters of the species calculated by two methods are generally in a good accordance to each other; while the internuclear distances Rb–Cl found with DFT/B3P86 are longer by 0.02–0.04 Å than those found with MP2 method. Among the species considered, for the  $Rb_3Cl_3$  molecule two isomers, hexagonal  $C_{3v}$  and butterfly-shaped  $C_{2v}$ , were proved to exist; the latter was evaluated to be more abundant in vapour. When compare the  $Rb_3Cl_3$  with  $Rb_3F_3$  studied previously, alike features may be noted (including the existence of two isomers). The results obtained for the heptaatomic ions show similarities between the respective properties of positive and negative ions.

## Authors' Contributions

All authors participate well in all steps including

computation, data analysis and manuscript preparation towards production of this work.

## Acknowledgment

The authors are very thankful to the Tanzania Commission for Science and Technology (COSTECH) through The Nelson Mandela African Institution of science and Technology for supporting and sponsoring this research work.

## Appendix

Tables A1 to A5 contain the thermodynamic functions of the ionic and molecular clusters; trimer  $Rb_3F_3$ , tetramer  $Rb_4Cl_4$ , and heptaatomic  $Rb_4Cl_3^+$  and  $Rb_3Cl_4^-$ . The tables include absolute temperature  $T$  in K, molar heat capacity  $c_p^\circ$ , Gibbs reduced free energy  $\Phi^\circ$ , and entropy  $S^\circ$  which are given in  $J\ mol^{-1}\ K^{-1}$ , and enthalpy increment  $H^\circ(T) - H^\circ(0)$  in  $kJ\ mol^{-1}$ .

**Table A1.** Thermodynamic functions of the  $Rb_3Cl_3$ ,  $C_{2v}$  isomer:

$T$	$c_p^\circ$	$S^\circ$	$H^\circ(T) - H^\circ(0)$	$\Phi^\circ$
298.15	130.24	514.540	33.025	403.718
700	132.51	626.923	85.999	504.067
800	132.64	644.626	99.257	520.555
900	132.71	660.253	112.524	535.226
1000	132.78	674.239	125.799	548.440
1100	132.82	686.896	139.079	560.461
1200	132.86	698.455	152.363	571.486
1300	132.89	709.090	165.649	581.668
1400	132.91	718.938	178.939	591.124
1500	132.93	728.108	192.230	599.955

**Table A2.** Thermodynamic functions of the  $Rb_3Cl_3$ ,  $D_{3h}$  isomer:

$T$	$c_p^\circ$	$S^\circ$	$H^\circ(T) - H^\circ(0)$	$\Phi^\circ$
298.15	130.23	516.663	33.245	405.102
700	132.51	629.039	86.216	505.873
800	132.63	646.742	99.474	522.400
900	132.70	662.368	112.741	537.100
1000	132.76	676.355	126.016	550.339
1100	132.84	689.012	139.296	562.379
1200	132.83	700.570	152.579	573.421
1300	132.81	711.205	165.866	583.616
1400	132.89	721.053	179.155	593.085
1500	132.92	730.223	192.446	601.926

**Table A3.** Thermodynamic functions of the  $Rb_4Cl_4$ ,  $T_d$  isomer:

$T$	$c_p^\circ$	$S^\circ$	$H^\circ(T) - H^\circ(0)$	$\Phi^\circ$
298.15	178.92	570.693	43.797	423.724
700	182.18	725.158	116.611	558.571
800	182.35	749.497	134.838	580.950
900	182.47	770.982	153.079	600.894
1000	182.56	790.212	171.331	618.881
1100	182.63	807.615	189.590	635.260
1200	182.67	823.507	207.854	650.295
1300	182.69	838.129	226.123	664.188
1400	182.74	851.670	244.394	677.103
1500	182.75	864.278	262.669	689.165



**Table A4.** Thermodynamic functions of the  $Rb_4Cl_3^+$ ,  $C_{3v}$  isomer.

$T$	$c_p^\circ$	$S^\circ$	$H^\circ(T)-H^\circ(0)$	$\Phi^\circ$
298.15	154.80	556.647	38.787	426.489
700	157.39	690.161	101.719	544.848
800	157.52	711.187	117.465	564.356
900	157.64	729.746	133.222	581.722
1000	157.70	746.357	148.988	597.369
1100	157.73	761.388	164.759	611.607
1200	157.77	775.115	180.534	624.670
1300	157.82	787.745	196.313	636.735
1400	157.73	799.440	212.095	647.944
1500	157.77	810.330	227.878	658.411

**Table A5.** Thermodynamic functions of the  $Rb_3Cl_4^-$ ,  $C_{3v}$  isomer.

$T$	$c_p^\circ$	$S^\circ$	$H^\circ(T)-H^\circ(0)$	$\Phi^\circ$
298.15	154.92	546.945	38.729	416.983
700	157.42	680.513	101.683	535.252
800	157.54	701.542	117.431	554.753
900	431.62	720.103	133.190	572.114
1000	157.70	736.715	148.957	587.758
1100	157.77	751.748	164.729	601.994
1200	157.79	765.475	180.506	615.053
1300	157.80	778.106	196.286	627.117
1400	157.84	789.802	212.068	638.325
1500	157.92	800.692	227.852	648.791

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