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

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Abstract: The geometrical structure and the vibrational spectra of dimer Rb_2Cl_2, trimer Rb_3Cl_3, tetramer Rb_4Cl_4 molecules and heptaatomic $Rb_4Cl_3^+$, $Rb_3Cl_4^-$ 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 Rb_2Cl_2, distorted cube (T_d) for tetramer Rb_4Cl_4 and polyhedral (C_{3v}) for heptaatomic ions $Rb_4Cl_3^+$ and $Rb_3Cl_4^-$. For the trimer molecule Rb_3Cl_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 $Rb^+(RbCl)_n$ (n = 1–4) [22].

Previously the quantum chemical methods has been used to study tri- and pentaatomic ions Rb_2Cl^+, $RbCl_2^-$, $Rb_3Cl_2^+$, $Rb_2Cl_3^-$ [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 $\Delta_r H°(0)$ of the reactions which were calculated through the following equations:

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

$$\Delta_r H°(0) = \Delta_r E + \Delta_r \varepsilon \quad (2)$$

$$\Delta_r \varepsilon = {}^1/_2 hc(\sum \omega_{i\ prod} - \sum \omega_{i\ reactant}) \quad (3)$$

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

3. Results and Discussion

3.1. Monomer RbCl and dimer Rb_2Cl_2

The properties of the diatomic RbCl and dimer Rb_2Cl_2 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(Rb–Cl)	2.878	2.857	2.860	2.855	2.787 [37]
$-E$	484.32782	484.42116	484.38973	483.40565	
ω_e	219	222	221	228	228 [38] 233 [39]
μ_e	11.0	10.9	10.9	11.4	10.483 [40]
IE_{vert}	8.45	8.66	8.53	8.52	8.50 ± 0.03 [41] 8.3 ± 0.1 [42, 43]
IE_{ad}	8.17	8.38	8.25		
EA	0.58	0.67	0.60	0.49	0.543 ± 0.01 [44]

Notes: Here and hereafter, R_e is the equilibrium internuclear distance (Å), E is the total electron energy (au), ω_e is the fundamental frequency (cm^{-1}), μ_e is the dipole moment (D), IE_{vert} and IE_{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 cm^{-1} (2.7–3.9%) for DFT methods while MP2 result coincides with the experimental value [38]. The results for dipole moment (μ_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_{ad}) was obtained as the energy difference of the $RbCl^+$ ion and neutral molecule where the internuclear separation R_e(Rb–Cl) was optimized both for neutral and ionic species and vertical ionization energy (IE_{vert}) was obtained as the energy difference of the $RbCl^+$ ion and neutral molecule where the internuclear separation R_e(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_{ad} by MP2 method was not calculated in this study.

For the dimer molecule Rb_2Cl_2, a planar cyclic structure of D_{2h} symmetry (Fig. 1*a*) 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 Rb_2Cl_2 indicates the rigidity of the structure; the lowest frequency being about 50 cm^{-1}.

In the IR spectrum, three vibrational modes ω_4, ω_5, and ω_6 have nonzero intensities but due to overlapping of ω_5 and ω_6 only two peaks could be seen which are asymmetrical stretching 171 cm^{-1} and wagging 52 cm^{-1} (MP2).

Based on results for the RbCl and Rb_2Cl_2 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_2Cl_2.*

Property	B3LYP5	B3P86	B3PW91	MP2	Ref. data
R_e(Rb–Cl)	3.081	3.053	3.062	3.032	2.989 [45][a]
α_e(Cl–Rb–Cl)	87.7	87.9	87.8	88.6	89.5 [45][a]
$-E$	968.71721	968.90454	968.84018	966.87305	
$\Delta_r E$	161.6	163.4	159.4	162.1	
$\Delta_r H°$	159.9	161.6	157.8	160.1	164±11 [22] 172.4 [46]
ω_1 (A_g)	158	163	161	172	
ω_2 (A_g)	66	64	66	68	
ω_3 (B_{1g})	135	138	135	153	
ω_4 (B_{1u})	49	48	49	52	
ω_5 (B_{2u})	155	158	155	171	
ω_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: [a]The MP2 calculation. Here and hereafter, α_e is the valence angle (deg). $\Delta_r E$ and $\Delta_r H°(0)$ are the energy and enthalpy of the dissociation reaction $Rb_2Cl_2 \rightleftharpoons 2RbCl$ (kJ mol^{-1}), I_i are the infrared intensities (D^2·amu^{-1}·Å^{-2}). The reducible vibration representation reduces to $\Gamma = 2A_g + B_{1g} + B_{1u} + B_{2u} + B_{3u}$.

3.2. Trimers Rb_3Cl_3 and tetramer Rb_4Cl_4

For the trimer molecule Rb_3Cl_3, 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. 1*b* and 1*c*) were confirmed to be equilibrium. The results are shown in Table 3.

Table 3. *Properties of trimer Rb_3Cl_3 molecule, hexagonal (D_{3h}) and butterfly-shaped (C_{2v}).*

Rb_3Cl_3 (D_{3h})			Rb_3Cl_3 (C_{2v})		
Property	**B3P86**	**MP2**	**Property**	**B3P86**	**MP2**
R_e(Rb–Cl)	3.051	3.032	R_{e1}(Rb_1–Cl_4)	2.997	2.982
			R_{e2}(Rb_3–Cl_5)	3.132	3.105
			R_{e3}(Rb_2–Cl_6)	3.093	3.068
			R_{e4}(Rb_3–Cl_6)	3.386	3.295
α_e(Rb–Cl–Rb)	117.9	119.5	α_e(Rb_2–Cl_5–Rb_3)	91.8	91.9
β_e(Cl–Rb–Cl)	122.1	120.5	β_e(Cl_4–Rb_1–Cl_6)	95.4	93.9
$-E$	1453.37224	1451.29449	$-E$	1453.37325	1451.29818
			$-\Delta_r E_{iso}$	2.6	9.7
ω_1 (A_1')	176	191	ω_1 (A_1)	177 (1.79)	185 (1.82)
ω_2 (A_1')	126	127	ω_2 (A_1)	128 (0.02)	135 (0.03)
ω_3 (A_1')	58	84	ω_3 (A_1)	90 (0.25)	102 (0.44)
ω_4 (E')	181	193	ω_4 (A_1)	73 (0.24)	85 (0.07)
ω_5 (E')	134	142	ω_5 (A_1)	55 (1.21)	57 (1.23)
ω_6 (E')	21	23	ω_6 (A_1)	50 (0.03)	51 (0.01)
ω_7 (A_2'')	46	48	ω_7 (A_2)	28 (0)	28 (0)
ω_8 (E'')	23	24	ω_8 (B_1)	8 (0.01)	13 (0.02)
I_4	3.94	3.98	ω_9 (B_2)	188 (1.25)	200 (1.38)
I_5	0.82	0.78	ω_{10} (B_2)	172 (0.45)	181 (0.26)
I_7	1.40	1.45	ω_{11} (B_2)	150 (1.03)	162 (1.08)
I_8	0.50	0.52	ω_{12} (B_2)	53 (0.19)	53 (0.19)
			μ_e	9.8	10.4

Notes: $\Delta_r E_{iso} = E(C_{2v}) - E(D_{3h})$ is the relative energy of the butterfly-shaped isomer regarding the hexagonal one (kJ mol^{-1}). The reducible vibration representations for Rb_3F_3 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^{2}amu^{-1}Å^{-2}).

For the hexagonal isomer (D_{3h}), one internuclear distance R_e(Rb–Cl) and one valence angle α_e(Rb–Cl–Rb) or β_e(Cl–Rb–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 α_e(Rb_2–Cl_5–Rb_3) and β_e(Cl_4–Rb_1–Cl_6) are used for the description. The butterfly-shaped configuration has lower energy, by 2.6 kJ mol^{-1} (DFT) and 10.0 kJ mol^{-1} (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 $\Delta_r E_{iso}$ (MP2) for the isomerization reaction Rb_3Cl_3 (D_{3h}) ⇌ Rb_3Cl_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.

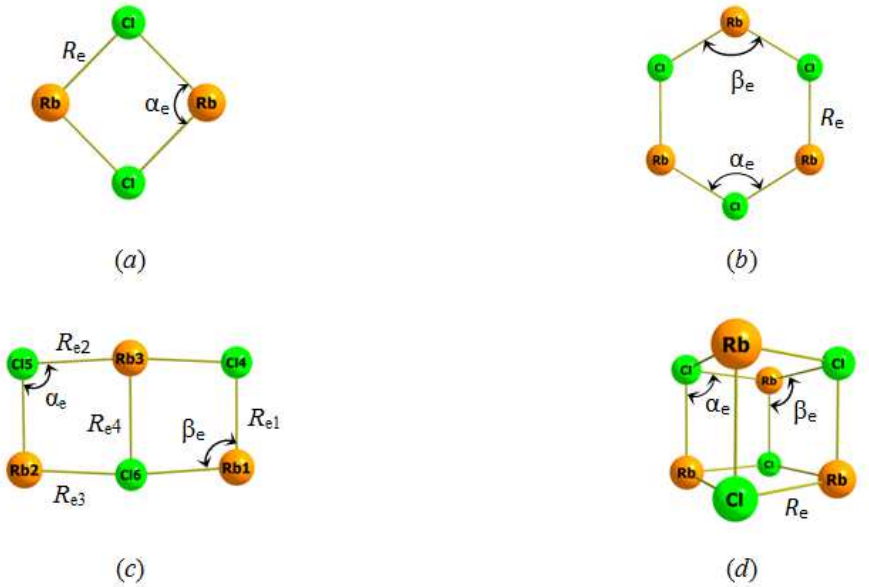


Figure 1. *Equilibrium geometric structures of molecules: (a) Rb_2Cl_2 (D_{2h}); (b) Rb_3Cl_3 (D_{3h}); (c) Rb_3Cl_3 (C_{2v}); (d) Rb_4Cl_4 (T_d).*

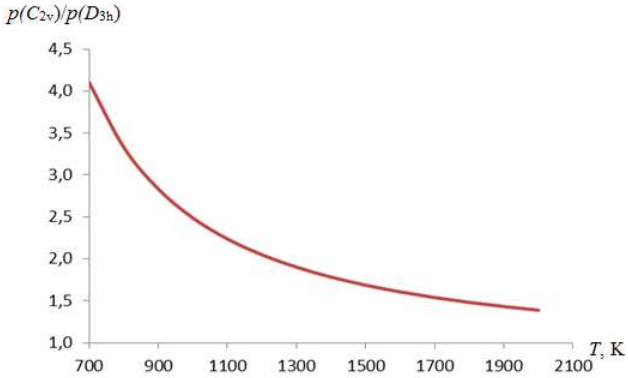
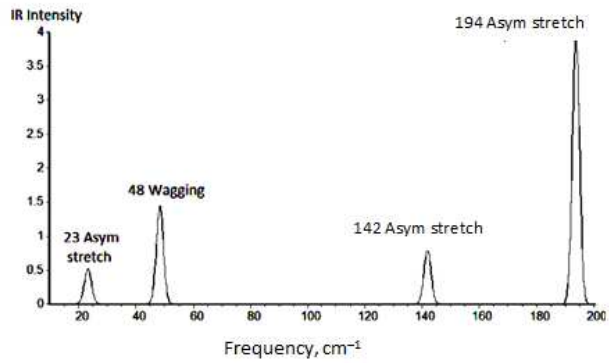


Figure 2. *Temperature dependence of relative amount of the C_{2v} isomer regarding to D_{3h} isomer of trimer Rb_3Cl_3 molecule.*

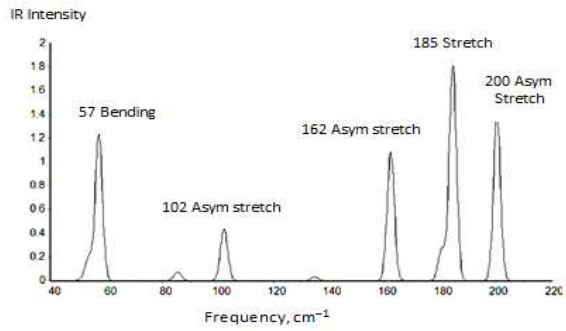
The IR spectra of both isomers of Rb_3Cl_3 molecule are shown in Fig. 3. The most intensive bands correspond to the stretching vibration modes and bending modes have lower intensities.

When comparing the properties of Rb_3Cl_3 with Rb_3F_3 molecule, a similarity may be noted: the same two isomers were revealed for Rb_3F_3 [21] and the butterfly-shaped isomer was predominant in that case as well.

For the tetramer molecule Rb_4Cl_4, the geometrical configuration considered was cube with T_d symmetry (Fig. 1*d*) 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 Rb_3Cl_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
α_e(Rb–Cl–Rb)	88.6	89.1
β_e(Cl–Rb–Cl)	91.4	90.9
$-E$	1937.87064	1935.11485
ω_1 (A_1)	138	145
ω_2 (A_1)	80	80
ω_3 (E)	119	128
ω_4 (E)	51	61
ω_5 (T_1)	116	127
ω_6 (T_2)	141	151
ω_7 (T_2)	137	146
ω_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 α_e(Rb–Cl–Rb) or β_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 ω_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, α_e(Rb_2–Cl_5–Rb_3), β_e(Rb_1–Cl_4–Rb_3) and γ_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^{-1} and 83 kJ mol^{-1} 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
α_e(Cl_6–Rb_2–Cl_7)	87.8	86.6	α_e(Rb_2–Cl_5–Rb_3)	84.7	85.1
β_e(Cl_5–Rb_1–Cl_7)	85.3	84.5	β_e(Rb_1–Cl_4–Rb_3)	83.0	83.8
γ_e(Rb_1–Cl_6–Rb_4)	89.2	89.9	γ_e(Cl_4–Rb_2–Cl_7)	91.2	90.9
$-E$	1477.41200	1475.10172	$-E$	1913.72426	1911.20087
ω_1 (A_1)	138 (0.61)	148 (0.82)	ω_1 (A_1)	138 (0.04)	146 (0.31)
ω_2 (A_1)	116 (0.91)	120 (0.71)	ω_2 (A_1)	134 (1.44)	141 (1.17)
ω_3 (A_1)	75 (0.06)	75 (0.07)	ω_3 (A_1)	72 (0.15)	74 (0.13)
ω_4 (A_1)	37 (0.15)	38 (0.19)	ω_4 (A_1)	50 (0.46)	51 (0.51)
ω_5 (A_2)	149 (0)	164 (0)	ω_5 (A_2)	126 (0)	138 (0)
ω_6 (E)	169 (3.28)	182 (3.30)	ω_6 (E)	147 (3.74)	157 (3.92)
ω_7 (E)	125 (1.56)	133 (1.52)	ω_7 (E)	132 (1.60)	140 (1.44)
ω_8 (E)	100 (0.02)	108 (0.06)	ω_8 (E)	108 (0.06)	120 (0.04)
ω_9 (E)	51 (0.08)	51 (0.08)	ω_9 (E)	54 (0.06)	54 (0.04
ω_{10} (E)	29 (0.10)	29 (0.12)	ω_{10} (E)	31 (0.26)	31 (0.28)

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

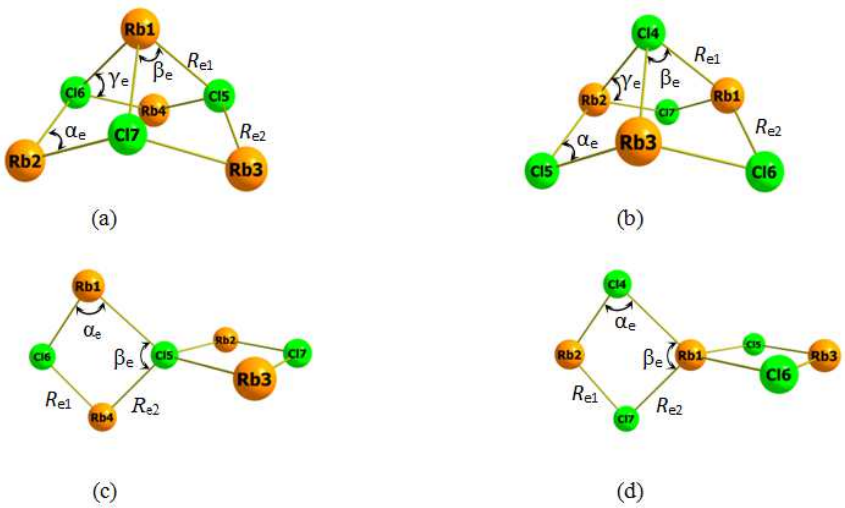
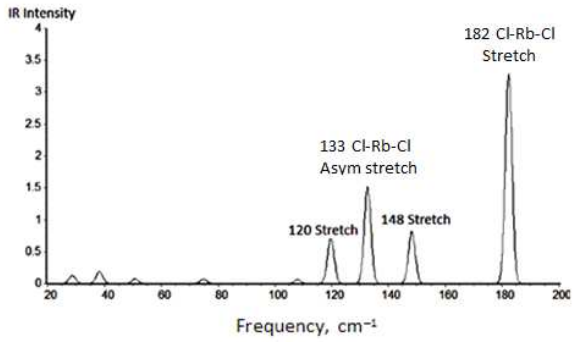
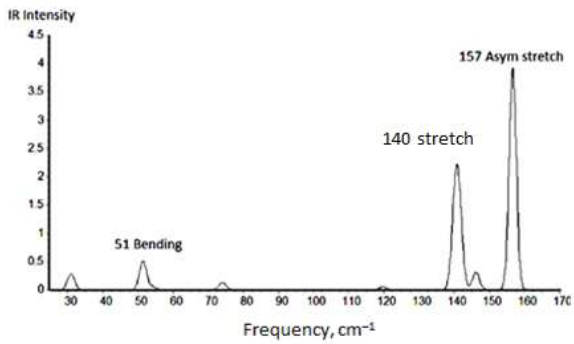


Figure 4. *Geometric structures of heptaatomic ions: polyhedral of D_{3h} symmetry (a) $Rb_4Cl_3^+$ (b) $Rb_3Cl_4^-$: two cycled with the mutually perpendicular planes of D_{2d} symmetry (c) $Rb_4Cl_3^+$ (d) $Rb_3Cl_4^-$.*

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.

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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 $c_p°$, Gibbs reduced free energy $\Phi°$, and entropy $S°$ which are given in J mol^{-1} K^{-1}, and enthalpy increment $H°(T)–H°(0)$ in kJ mol^{-1}.

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

T	$c_p°$	$S°$	$H°(T)–H°(0)$	$\Phi°$
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	$c_p°$	$S°$	$H°(T)–H°(0)$	$\Phi°$
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	$c_p°$	$S°$	$H°(T)–H°(0)$	$\Phi°$
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	$c_p°$	*S°*	*H°(T)–H°(0)*	*Φ°*
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	$c_p°$	*S°*	*H°(T)–H°(0)*	*Φ°*
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

References

[1] Cramer, C. J. (2004), *Essentials of computational chemistry: theories and models*. John Wiley & Sons Ltd, 2nd Ed, USA.

[2] Khanna, S. and Jena P., *Assembling crystals from clusters.* Phys. Rev. lett. 1993. 71(1): p. 208.

[3] Khanna, S. and Jena P., *Atomic clusters: Building blocks for a class of solids.* Phys. Rev. B. 1995. 51(19): p. 13705.

[4] Sarkas, H. W., Kidder, L. H., and Bowen, K. H., *Photoelectron spectroscopy of color centers in negatively charged cesium iodide nanocrystals*. J. Chem. Phys. 1995. 102(1): p. 57–66.

[5] Alexandrova, A. N., Boldyrev, A. I., Fu, Y. J., Yang, X., Wang, X. B., and Wang, L. S., *Structure of the Na_xCl_{x+1} (x= 1–4) clusters via ab initio genetic algorithm and photoelectron spectroscopy.* J. Chem. Phys. 2004. 121(12): p. 5709–5719.

[6] Castleman, A. and Bowen K., *Clusters: Structure, energetics, and dynamics of intermediate states of matter.* J. Phys. Chem. 1996. 100(31): p. 12911–12944.

[7] Castleman Jr, A. and Khanna S., *Clusters, Superatoms, and Building Blocks of New Materials.* J. Phys. Chem. 2009. 113(7): p. 2664–2675.

[8] Pogrebnoi, A. M., Pogrebnaya, T. P., Kudin, L. S., and Tuyizere, S., *Structure and thermodynamic properties of positive and negative cluster ions in saturated vapour over barium dichloride*. Mol. Phys. 2013. 111(21): p. 3234–3245.

[9] Hishamunda, J., Girabawe, C., Pogrebnaya, T., and Pogrebnoi, A., *Theoretical study of properties of Cs_2Cl^+, $CsCl_2^-$, $Cs_3Cl_2^+$, and $Cs_2Cl_3^-$ ions: Effect of Basis set and Computation Method.* Rwanda Journal. 2012. 25(1): p. 66–85.

[10] Fernandez-Lima, F. A., Nascimento, M. A. C., and da Silveira E. F., *Alkali halide clusters produced by fast ion impact. Nuclear Instruments and Methods in Physics Research Section B*: Beam Interactions with Materials and Atoms, 2012. 273: p. 102–104.

[11] Rao, B., Khanna S., and Jena P., *Designing new materials using atomic clusters.* J. Clust. Sc. 1999. 10(4): p. 477–491.

[12] Chupka, W. A., *Dissociation energies of some gaseous alkali halide complex ions and the hydrated ion $K(H_2O)^+$.* J. Chem. Phys. 1959. 30(2): p. 458–465.

[13] Huh, S. and Lee G., *Mass spectrometric study of negative, positive, and mixed KI cluster ions by using fast Xe atom bombardment.* J. Kor. Phys. Soc. 2001. 38(2): p. 107–110.

[14] Honig, A., Stitch, M., and Mandel, M., *Microwave Spectra of CsF, CsCl, and CsBr*. Phys. Rev. 1953. *92*(4), 901.

[15] Honig, A., Mandel, M., Stitch, M., and Townes, C., *Microwave spectra of the alkali halides.* Phys. Rev. 1954. 96(3), 629.

[16] Fabricand, B. P., Carlson, R., Lee, C. A., and Rabi, I., *Molecular Beam Investigation of Rotational Transitions. II. The Rotational Levels of KBr and Their Hyperfine Structure.* Phys. Rev. 1953. 91(6), 1403.

[17] Aguado, A., *An ab initio study of the structures and relative stabilities of doubly charged $[(NaCl)_m(Na)_2]_2^+$ cluster ions*. J. Phys. Chem. B. 2001. 105(14): p. 2761–2765.

[18] Costa, R., Pogrebnaya T., and Pogrebnoi A., *Structure and vibrational spectra of cluster ions over rubidium iodide by computational chemistry.* Pan African Conference on Computing and Telecommunications in Science (PACT). IEEE. 2014. PACTAT01114: p. 52–55; doi: 10.1109/SCAT.2014.7055136.

[19] Mwanga, S. F., Pogrebnaya T. P., and Pogrebnoi A. M., *Structure and properties of molecular and ionic clusters in vapour over caesium fluoride.* Mol. Phys. 2015: p. 1–16.

[20] Pogrebnaya, T. P., Hishamunda, J. B., Girabawe, C., and Pogrebnoi, A. M., *Theoretical study of structure, vibration spectra and thermodynamic properties of cluster ions in vapors over potassium, rubidium and cesium chlorides* Chemistry for Sustainable Development. 2012, Springer. p. 353–366.

[21] Abubakari, I., Pogrebnaya, T., Pogrebnoi. A., *Molecular and Ionic Clusters of Rubidium Fluoride: Theoretical Study of Structure and Vibrational Spectra*. Inter. J. Comp. Theor. Chem. 2015. 3(5). p. 34-44. doi: 10.11648/j.ijctc.20150305.11

[22] Motalov, V., Pogrebnoi, A., and Kudin, L., *Molecular and Ionic Associates in Vapours of Rubidium Chloride*. Russ. J. Phys. Chem. (Zhurnal Fizicheskoi Khimii), 2001. *75*. p. 1547-1552.

[23] Becke, A. D., *Density-functional thermochemistry. III. The role of exact exchange.* J. Chem. Phys. 1993. 98(7): p. 5648–5652.

[24] Perdew, J. P. and Zunger A., *Self-interaction correction to density-functional approximations for many-electron systems.* Phys. Rev. B. 1981. 23(10): p. 5048.

[25] Perdew, J., Phys. Rev. B. 1986, 33, 8822–8824; b) Perdew, J. P., Phys. Rev. B. 1986. 34: p. 7406–7406.

[26] Perdew, J. P., *Density-functional approximation for the correlation energy of the inhomogeneous electron gas.* Phys. Rev. B. 1986. 33(12): p. 8822.

[27] Schmidt, M. W., Baldridge, K. K., Boatz, J. A., Elbert, S. T., Gordon, M. S., Jensen, J. H., Koseki, S., Matsunaga, N., Nguyen, K. A., Su, S., Windus, T. L., Dupuis, M., Montgomery, J. A., *General Atomic and Molecular Electronic Structure System.* J. Comput. Chem. 1993. 14: p. 1347-1363; doi:10.1002/jcc.540141112.

[28] Granovsky, A. A., Firefly version 8.1.0, www http://classic.chem.msu.su/gran/firefly/index.html

[29] Zhurko G. A., Zhurko D. A., Chemcraft Version 1.7 (build 132). HTML: www.chemcraftprog.com.

[30] Bode, B. M., and Gordon, M. S., MacMolPlt version 7.4.2. J. Mol. Graphics and Modeling, 1998. 16: p. 133–138. Available: http://www.scl.ameslab.gov/MacMolPlt/.

[31] Leininger, T., Nicklass, A., Küchle, W., Stoll, H., Dolg, M., and Bergner, A., *The accuracy of the pseudopotential approximation: Non-frozen-core effects for spectroscopic constants of alkali fluorides XF (X= K, Rb, Cs).* Chem. Phys. Lett. 1996. 255(4): p. 274–280.

[32] EMSL basis set exchange website: https://bse.pnl.gov/bse/portal

[33] Kendall, R. A., Dunning Jr, T. H., and Harrison, R. J., *Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions.* J. Chem. Phys. 1992. 96(9): p. 6796–6806.

[34] Feller, D., *The role of databases in support of computational chemistry calculations.* J. Comp. Chem. 1996. 17(13): p. 1571–1586.

[35] Schuchardt, K. L., Didier, B. T., Elsethagen, T., Sun, L., Gurumoorthi, V., Chase, J., and Windus, T. L., *Basis set exchange: a community database for computational sciences.* J. Chem. Info. Mod. 2007. 47(3): p. 1045–1052.

[36] Tokarev, K. L., "OpenThermo", v.1.0 Beta 1 (C) ed. http://openthermo.software.informer.com/, 2007–2009.

[37] Krasnov, K. S., Philippenko, N. V., Bobkova, V. A., Lebedeva, N. L., Morozov, E. V., Ustinova, T. I., and Romanova, G. A., *Molekulyarnye postoyannye neorganicheskikh soedineniy (Handbook Molecular constants of inorganic compounds).* 1979.

[38] Rice, S. A., and Klemperer, W., *Spectra of the alkali halides. II. The infrared spectra of the sodium and potassium halides, RbCl and CsCl.* J. Chem. Phys., 1957, 27, p. 573–579.

[39] Clouser, P. L., and Gordy, W., *Millimeter-wave molecular-beam spectroscopy: alkali chlorides.* Phys. Rev., 1964, 134, 863.

[40] Hebert, A., Lovas, F., Melendres, C., Hollowell, C., Story Jr, T., and Street Jr, K., *Dipole moments of some alkali halide molecules by the molecular beam electric resonance method.* J. Chem. Phys. 1968. 48(6): p. 2824.

[41] Berkowitz, J., *Photoionization mass spectrometry photoelectron spectroscopy of high temperature vapour*. Adv. High Temp. Chem., 1971, 3, 123

[42] Potts, A. W.; Williams, T. A.; Price, W. C., *Photoelectron spectra and electronic structure of diatomic alkali halides*. Proc. Roy. Soc. London A, 1974, 341, 147

[43] Potts, A. W., and Price, W. C., *Photoelectron studies of ionic materials using molecular beam techniques*. Phys. Scr. 1977, 16, 191

[44] Miller, T. M., Leopold, D. G., Murray, K. K., Lineberger, W. C., *Electron Affinities of the Alkali Halides and the Structure of their Negative Ions*. J. Chem. Phys., 1986, 85, 5, 2368; doi:10.1063/1.451091

[45] Hargittai, M., *Molecular structure of metal halides.* Chem. Rev. 2000. 100(6): p. 2233–2302

[46] L. V. Gurvich, V. S. Yungman, G. A. Bergman, I. V. Veitz, A. V. Gusarov, V. S. Iorish, V. Y. Leonidov, V. A. Medvedev, G. V. Belov, N. M. Aristova, L. N. Gorokhov, O. V. Dorofeeva, Y. S. Ezhov, M.E. Efimov, N. S. Krivosheya, I. I. Nazarenko, E. L. Osina, V. G. Ryabova, P. I. Tolmach, N. E. Chandamirova, E. A. Shenyavskaya, *Thermodynamic Properties of individual Substances. Ivtanthermo for Windows Database on Thermodynamic Properties of Individual Substances and Thermodynamic Modeling Software.* Version 3.0 (Glushko Thermocenter of RAS, Moscow, 1992–2000).

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