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Theoretical study of properties of Cs_2Cl^+, $CsCl_2^-$, $Cs_3Cl_2^+$, and $Cs_2Cl_3^-$ ions: Effect of Basis set and Computation Method

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Abstract

Theoretical study of properties of Cs_2Cl^+, $CsCl_2^-$, $Cs_3Cl_2^+$ *and* $Cs_2Cl_3^-$ *ions has been performed using the density functional theory (DFT/B3LYP) and the second order Møller-Plesset perturbation theory (MP2). Two triple-zeta basis sets, the midsized B1 and the extended one B2, have been used. Equilibrium structure, vibrational spectra, energies and enthalpies of dissociation reactions of the ions have been found. The effect of the basis set size and the computation method on the results has been analyzed. The MP2 method with the extended basis B2 set was accepted as the more accurate among the others. For the triatomic ions* Cs_2Cl^+ *and* $CsCl_2^-$*, the equilibrium structure has been found to be linear. For the pentaatomic ions, three isomeric forms were considered. The most abundant isomer in saturated vapor was found to be the angular V-shaped of* C_{2v} *symmetry for* $Cs_3Cl_2^+$ *and the linear of* $D_{\infty h}$ *symmetry for* $Cs_2Cl_3^-$*. Thermodynamic functions of the ions were computed and applied to the treatment of experimental mass spectrometric data. Enthalpies of formation* $\Delta_f H^o(0\ K)$ *were determined (in kJ/mol):*
51 ± 4 (Cs_2Cl^+)*, −622 ± 3* ($CsCl_2^-$)*, −301 ± 8* ($Cs_3Cl_2^+$)*, −975 ± 6* ($Cs_2Cl_3^-$)*.*

Key-Words: *geometrical structure, vibrational frequencies, thermodynamic properties*

1. Introduction

It has been found experimentally in mass spectrometric studies that positive and negative cluster ions exist in vapors over cesium chloride (Pogrebnoi, et al., 2002) and other alkali metal halides (Motalov, et al., 2001; Kudin, et al., 1990; Gusarov, 1986; Chupka, 1959). The ions M_2X^+, MX_2^-, $M_3X_2^+$ and $M_2X_3^-$ (M is an alkali metal; X is halogen) were recorded at elevated temperatures in these studies.

Similar charged particles were proved to be important in different applications such as ion thrusters (Patterson, 2008), magneto-hydrodynamic (MHD) generators, ion implantation (Woolley, 1997; Lieberman and Lichtenberg, 1994), aerospace investigations (Huenecke, 2002) etc. For example, in ions thrusters, accelerated ions beams generate a propellant force. The ions accelerating systems vary but they are generally based on mass to charge ratio of ions. It is then clear that the heavier ions are the bigger is the propellant force. It should be noted that recent space technology is moving from lighter hydrogen and lithium ions to relatively heavier ions.

Mass spectrometric study is usually used for investigation of ions in gaseous phase. For the treatment of the experimental mass spectrometric data, the thermodynamic functions of ions and molecules are needed. Geometry structure and vibrational frequencies are necessary for the computation of the thermodynamic functions. Meanwhile, the experimental data about the structure and spectra of these cluster ions are unavailable. Comparison method based on ionic model which have been used earlier by Gusarov (1986), showed that the ions considered here possess the linear structure.

Quantum mechanical methods provide trustworthy results now. Previously the quantum mechanical calculations were performed by Pogrebnaya et al., (2007, 2008, 2010) for sodium halides ions Na_2X^+, NaX_2^-, $Na_3X_2^+$, and $Na_2X_3^-$ (X = F, Cl, Br and I). The different theoretical approximations such as Density Functional Theory, Möller–Plesset perturbation theory, Configuration Interaction method with various atomic basis sets have been used. It was found that the theoretical level has an effect on the results about the geometrical structure and vibrational frequencies of the ions. To be sure about the correctness of the calculated properties, the analysis of the applied approximation is significant.

The aims of the present work were as follows:

- to perform theoretical study of the properties of the tri- and pentaatomic ions Cs_2Cl^+, $CsCl_2^-$, $Cs_3Cl_2^+$ and $Cs_2Cl_3^-$;
- to analyze the effect of basis set and computation method on the results;
- to choose the theoretical approximation which provides the dependable data;
- to determine the thermodynamic properties of the ions on the base of data obtained.

2. Methodology

The calculations were performed using PC GAMESS version 7.1.C (Granovsky, 2010) of the GAMESS software package (Schmidt, et al., 1993) and implementing the following methods: electron density functional theory (DFT) with the Becke–Lee–Yang–Parr functional (B3LYP5), the second order and fourth order Möller–Plesset perturbation theory (MP2 and MP4). Two basis sets have been utilized. The first basis set denoted as B1 was midsized: the McLean-Chandler full-electron basis set (7s6p1d) for Cl (Schmidt, et al., 1993) and the relativistic effective core potential with valence correlation consistent cc-pVTZ basis set (5s4p1d) for Cs (Feller, 1996; Schuchardt, et al., 2007). The second basis set denoted as B2 was extended: the full-electron basis set cc-pVTZ (6s5p3d2f) for Cl and valence cc-pVTZ (6s5p4d1f) for Cs (Feller, 1996; Schuchardt, et al., 2007). The combination of the two methods (DFT and MP2) and two basis sets (B1 and B2) provided us with four theoretical approximations: DFT B1, MP2 B1, DFT B2, and MP2 B2 to optimize geometric parameters of the ions and calculate vibrational frequencies. Further computation with higher theoretical level MP4 B2 was performed to obtain more accurate values of dissociation energy of the ions. In the calculations with MP2 and MP4 methods, the 1s, 2s, and 2p atomic orbitals of Cl were frozen.

3. Results and discussion

CsCl molecule

The properties of CsCl molecule such as equilibrium internuclear distance, normal vibrational frequency, dipole moment, and ionization potential, were computed using the four approximations. These calculated values are compared with the reference experimental data in Table 1.

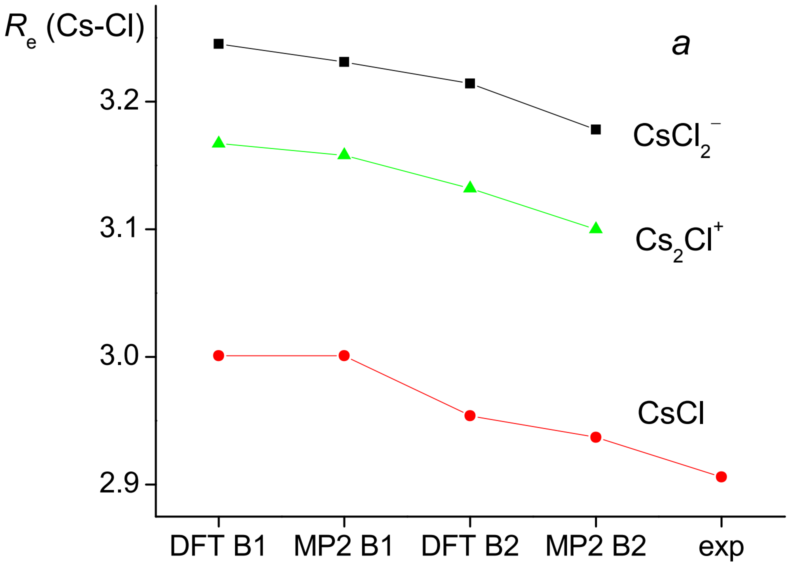
Table 1: Calculated and experimental parameters for CsCl molecule

Property	DFT B1	MP2 B1	DFT B2	MP2 B2	Experimental
R_e(Cs−Cl), Å	3.001	3.001	2.954	2.937	2.906
ω_e, cm^{-1}	202	205	206	209	214
μ_e, D	11.3	11.7	10.4	10.7	10.5
IP, eV	5.5	8.9	5.7	9.1	8.1 ± 0.2

R_e(Cs−Cl) is the equilibrium internuclear distance, ω_e is the frequency of normal vibration, μ_e is the dipole moment, IP is the ionization potential. The calculated value of IP was taken as the energy of the highest occupied MO. Experimental data were taken from (Krasnov, 1979; Kondrat'ev, 1974).

In the series DFT B1 – MP2 B1 – DFT B2 – MP2 B2, the theoretical value of the internuclear distance R_e(Cs–Cl) is decreasing systematically and approaches the experimental value, still it is overrated by 0.03 Å for the theoretical MP2 B2 result (Fig. 1a). The theoretical value of the vibrational frequency ω_e is increasing in this series, but it is underrated by 5 cm^{-1} (2.3%) for the MP2 B2 result. The dipole moment found either in DFT or MP2 method using the extended basis set B2 agrees with the reference value. The basis set B1 is not appropriate here. The ionization potentials obtained with MP2 method (both B1 and B2 basis sets) do not contradict to the reference value, but the results obtained with DFT method are much less (about 30%) than the experimental value.

Therefore, the molecular parameters of CsCl obtained with MP2 B2 method correspond better to the reference data compared with the results of the other three methods concerned. Thus, among the four methods, the MP2 B2 approximation gives the most appropriate data on properties of CsCl molecule and for the ions we suppose that it may also be the case.



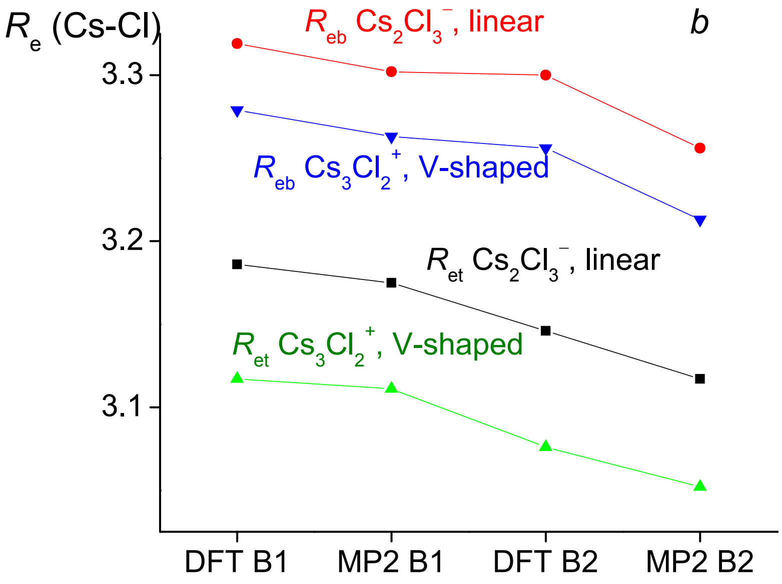


Figure 1: Equilibrium internuclear distances *R*e(Cs−Cl) in Å obtained with different methods: (*a*) for molecule CsCl, and thriatomic ions Cs2Cl+, CsCl2−; and (*b*) for pentaatomic ions Cs3Cl2+, Cs2Cl3−

Triatomic ions Cs_2Cl^+ and $CsCl_2^-$

The properties of the triatomic ions Cs_2Cl^+ and $CsCl_2^-$ such as equilibrium internuclear distance R_e(Cs–Cl), the normal vibrational frequencies ω_i and the intensities of the vibration in IR spectra A_i, obtained using these four theoretical methods, are represented in Table 2. According to all of the methods, the equilibrium structure of the ions is linear of $D_{\infty h}$ symmetry. In the series DFT B1 − MP2 B1 − DFT B2 − MP2 B2, the change in the equilibrium distance in Cs_2Cl^+ is similar to that in the $CsCl_2^-$ ion and in the CsCl molecule also (Fig. 1a). The frequencies of the ions expose no big change in their values and may be considered constant approximately in the series of the calculations with the exception of the deformational frequency ω_3 in the $CsCl_2^-$ ion. This frequency is small itself and seems to be quite sensitive to the applied theoretical level. It appears the uncertainty in the low deformational frequency is about 5 cm^{-1} and should be taken into account in the calculations of uncertainties of the thermodynamic functions. The IR intensities are to be considered as qualitative parameters only to show which vibration is more intensive or less intensive in the spectra. For instance, the antisymmetric valence vibration ω_2 (Σ_u^+) is more intensive than the deformation vibration ω_3 (Π_u) as for positive as for negative ions.

Table 2: Properties of the triatomic Cs_2Cl^+ and $CsCl_2^-$ ions

	Cs_2Cl^+			
Property	DFT B1	MP2 B1	DFT B2	MP2 B2
R_e(Cs–Cl)	3.167	3.158	3.132	3.100
E	−500.41426	−499.50723	−500.42355	−499.77527
ω_1 (Σ_g^+)	74	76	73	77
ω_2 (Σ_u^+)	201	205	196	209
ω_3 (Π_u)	39	34	34	38
A_2	1.93	1.83	2.17	2.08
A_3	1.05	1.10	0.87	0.91
	$CsCl_2^-$			
Property	DFT B1	MP2 B1	DFT B2	MP2 B2
R_e(Cs–Cl)	3.245	3.231	3.214	3.178
E	−940.67146	−939.42315	−940.68633	−939.67506
ω_1 (Σ_g^+)	138	140	139	143
ω_2 (Σ_u^+)	148	151	147	150
ω_3 (Π_u)	20	17	19	15
A_2	2.26	2.22	2.38	2.30
A_3	1.99	2.05	1.79	1.84

R_e(M–Cl) is the equilibrium internuclear distance, Å; E is the total electron energy, au; ω_i are the frequencies of normal vibrations, cm^{-1}; A_i are the IR intensities, $D^2amu^{-1}Å^{-2}$

Pentaatomic ions $Cs_3Cl_2^+$ and $Cs_2Cl_3^-$

For pentaatomic ions $Cs_3Cl_2^+$ and $Cs_2Cl_3^-$, several probable geometric configurations of the nuclei were considered as it follows: $D_{\infty h}$ linear symmetry, C_{2v} planar cyclic symmetry, and D_{3h} bipyramidal symmetry (Fig. 2). For each configuration the geometric parameters were optimized, and the frequencies of normal vibrations were calculated.

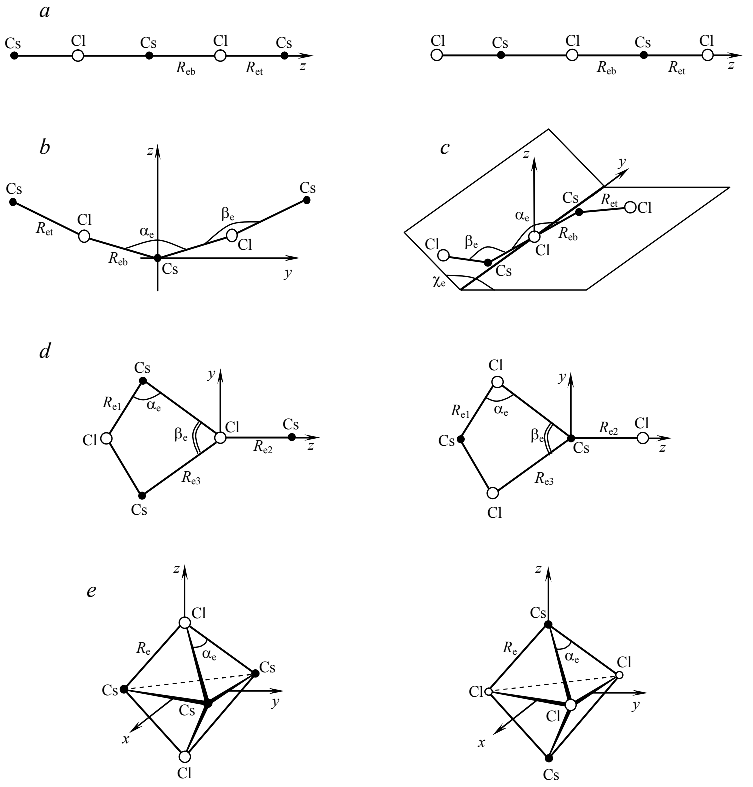


Figure 2: Isomers of the pentaatomic ions: (*a*) linear, (*b*) V-shaped, (c) nonplanar, (*d*) cyclic, and (*e*) bipyramidal

The results obtained for the linear structure are given in Table 3. However, for the positive ion $Cs_3Cl_2^+$, it was found the linear structure was not equilibrium as the frequency ω_7 (Π_u) was imaginary according to the calculations with the all four methods. The further optimization led to an angular V-shaped configuration of C_{2v} symmetry shown in Fig. 2b. The equilibrium structure has the central angle α_e(Cl−Cs−Cl) about 140° and actually linear fragments Cs−Cl−Cs, the parameters are given in Table 4. The decrease in energy by 0.2 – 0.5 kJ/mol compared with the linear structure was observed.

Table 3: Properties of the pentaatomic ions $Cs_3Cl_2^+$ and $Cs_2Cl_3^-$ of linear configuration $D_{\infty h}$ symmetry

	$Cs_3Cl_2^+$			
Property	DFT B1	MP2 B1	DFT B2	MP2 B2
R_{et}(Cs−Cl)	3.118	3.111	3.077	3.051
R_{eb}(Cs−Cl)	3.290	3.279	3.270	3.228
E	−980.83568	−979.21126	−980.85335	−979.65415
[illegible] (Σ_g^+)	198	203	197	206
[illegible] (Σ_g^+)	47	49	47	49
[illegible] (Σ_u^+)	192	198	189	200
[illegible] (Σ_u^+)	82	85	82	84
[illegible] (Π_g)	30	25	27	27
[illegible] (Π_u)	35	31	32	28
[illegible] (Π_u)	$5i$	$4i$	$4i$	$10i$
A_3	3.91	3.68	4.50	4.27
A_4	0.00	0.00	0.01	0.01
A_6	2.01	2.12	1.67	1.66
	$Cs_2Cl_3^-$			
Property	DFT B1	MP2 B1	DFT B2	MP2 B2
R_{et}(Cs−Cl)	3.186	3.175	3.146	3.117
R_{eb}(Cs−Cl)	3.319	3.302	3.300	3.256
E	−1421.09169	−1419.12589	−1421.11510	−1419.55305
[illegible] (Σ_g^+)	158	161	156	162
[illegible] (Σ_g^+)	52	55	52	53
[illegible] (Σ_u^+)	164	171	162	172
[illegible] (Σ_u^+)	154	157	152	158
[illegible] (Π_g)	11	7	6	(15) $12i$
[illegible] (Π_u)	25	21	22	23
[illegible] (Π_u)	10	5	7	(9) $8i$
A_3	1.93	1.96	1.12	1.44
A_4	2.27	2.09	3.53	2.98
A_6	2.29	2.60	1.89	1.55
A_7	0.76	0.55	0.79	-

R_{et}(Cs−Cl) and R_{eb}(Cs−Cl) are the terminal and bridge internuclear distances respectively; Å; E is the total electron energy, au; ω_i are the frequencies of normal vibrations, cm^{-1}; A_i are the IR intensities, $D^2amu^{-1}Å^{-2}$. The vibrational representation is $\Gamma = 2\Sigma_g^+ + 2\Sigma_u^+ + \Pi_g + 2\Pi_u$

As it seen in Table 4, in the rank DFT B1 − MP2 B1 − DFT B2 − MP2 B2, the change of the equilibrium distances R_{et}(Cs−Cl) and R_{eb}(Cs−Cl) in $Cs_3Cl_2^+$ is similar to that in the triatomic ions and in the molecule CsCl (Fig. 1). The values of the frequencies look like independent of the theory level except the lowest frequency ω_5 (A_1) which is very sensitive to the choice of the method. We consider the value of ω_5 = 10 cm^{-1} obtained by the MP2 B2 method as more appropriate.

Table 4: Properties of the $Cs_3Cl_2^+$ ion of V-shaped configuration

Property	DFT B1	MP2 B1	DFT B2	MP2 B2
R_{et}(Cs−Cl)	3.117	3.111	3.076	3.052
R_{eb}(Cs−Cl)	3.279	3.263	3.256	3.213
α_e(Cl−Cs−Cl)	138.5	138.2	142.3	141.1
β_e(Cs−Cl−Cs)	178.8	179.8	179.5	179.7
E	−980.83576	−979.21142	−980.85348	−979.65434
$E - E(D_{\infty h})$	−0.21	−0.42	−0.34	−0.50
[illegible]A_1)	199	205	199	208
[illegible]A_1)	56	57	55	56
[illegible]A_1)	39	34	35	35
[illegible]A_1)	37	33	34	35
[illegible](A_1)	6	5	5	10
[illegible]A_2)	80	83	80	86
[illegible]A_2)	29	24	27	28
[illegible]B_1)	193	199	191	201
[illegible]B_1)	30	23	27	28
μ_e	6.8	6.6	5.0	6.1

R_{et}(Cs−Cl) and R_{eb}(Cs−Cl) are the terminal and bridge internuclear distances respectively; Å; α_e and β_e are the valence angles in degrees; E is the total electron energy, au; $E - E(D_{\infty h})$ is the relative energy, kJ/mol. ω_i are the frequencies of normal vibrations, cm^{-1}; μ_e is the dipole moment, D. The vibrational representation is $\Gamma = 5A_1 + 2A_2 + 2B_1$

For the negative ion $Cs_2Cl_3^-$, the linear structure of $D_{\infty h}$ symmetry is the equilibrium one according to the results by the DFT B1, MP2 B1 and DFT B2 methods while the MP2 B2 calculation gave the imaginary frequencies ω_5 (Π_g) and ω_7 (Π_u). We continued the optimization to get the equilibrium configuration. The result was "slightly distorted" structure of C_2 symmetry with the valence angles of α_e(Cs−Cl−Cs) = 179.5°, β_e(Cl−Cs−Cl) = 177.4° and the torsion angle χ_e about 134° (Fig. 2c). The energy of the $Cs_2Cl_3^-$ with the C_2 symmetry appeared to be the same as for the linear structure of $D_{\infty h}$ symmetry though. Moreover the further analysis of thermodynamic properties calculated on the base of this structure gave us unreasonable results. Therefore we refused this "slightly distorted" structure and assumed that the equilibrium structure of $Cs_2Cl_3^-$ was linear of $D_{\infty h}$ symmetry. We estimated the values of ω_5 (Π_g) = 15 cm^{-1} and ω_7 (Π_u) = 9 cm^{-1} by comparative method using the results obtained for the similar $K_2Cl_3^-$ and $Rb_2Cl_3^-$ ions (Pogrebnaya, et al., 2012).

Other two structures, cyclic (C_{2v}) and bipyramidal (D_{3h}), were found to be equilibrium and the parameters are presented in Tables 5 and 6 accordingly. In the case of $Cs_3Cl_2^+$ ion, the relative energy of the cyclic isomer h_{iso} = *E*(*cyclic*) – *E*(*V-shaped*) is positive according to DFT method and negative according to MP2 method. For the $Cs_2Cl_3^-$ ion, the value of h_{iso} = *E*(*cyclic*) – *E*(*linear*) is negative in all four theoretical approximations. In addition, the values of h_{iso} are decreasing from B1 to B2 transition and from DFT to MP2 as well.

Table 5: Properties of the isomers of the pentaatomic ions with cyclic structure of C_{2v} symmetry

	$Cs_3Cl_2^+$			
Property	DFT B1	MP2 B1	DFT B2	MP2 B2
R_{e1}(Cs–Cl)	3.154	3.131	3.121	3.124
R_{e2}(Cs–Cl)	3.192	3.175	3.150	3.086
R_{e3}(Cs–Cl)	3.510	3.441	3.488	3.400
α_e	83.6	82.1	84.5	83.5
β_e	89.6	91.7	88.5	90.3
h_{iso}	5.23	−3.07	2.91	−6.04
[illegible] (A_1)	168	175	165	173
[illegible] (A_1)	146	153	146	156
[illegible] (A_1)	56	58	56	59
[illegible] (A_1)	41	42	39	42
[illegible] (B_1)	56	56	51	53
[illegible] (B_1)	20	18	17	19
[illegible] (B_2)	168	178	165	174
[illegible] (B_2)	85	95	82	92
[illegible] (B_2)	23	24	21	21
μ_e	9.0	9.3	8.1	8.4
	$Cs_2Cl_3^-$			
Property	DFT B1	MP2 B1	DFT B2	MP2 B2
R_{e1}(Cs–Cl)	3.174	3.149	3.140	3.164
R_{e2}(Cs–Cl)	3.239	3.229	3.195	3.103

R_{e3}(Cs–Cl)	3.543	3.478	3.531	3.446
α_e	89.4	90.7	87.6	87.9
β_e	84.2	83.7	85.4	85.8
h_{iso}	−2.94	−9.37	−3.94	−12.34
(A_1)	161	167	159	168
(A_1)	143	145	145	148
(A_1)	94	99	93	100
(A_1)	42	41	41	38
(B_1)	43	42	41	40
(B_1)	16	13	15	15
(B_2)	152	158	149	160
(B_2)	80	86	77	87
(B_2)	30	29	30	30
μ_e	9.7	10.2	8.5	8.8

R_{e1}(Cs–Cl), R_{e2}(Cs–Cl), R_{e3}(Cs–Cl) are the internuclear distances, Å; α_e and β_e are the valence angles in degrees (Fig. 2); h_{iso} is the relative energy of isomer, kJ/mol; ω_i are the frequencies of normal vibrations, cm^{-1}; μ_e is the dipole moment, D. The vibrational representation is $\Gamma = 4A_1 + 2B_1 + 3B_2$

For the bipyramidal structure of both ions, the relative energy h_{iso} is negative as a rule. Therefore the bipyramidal isomers are energetically more stable than V-shaped isomer of $Cs_3Cl_2^+$ or the linear isomer of $Cs_2Cl_3^-$.

Table 6: Properties of the isomers of the pentaatomic ions with bipyramidal structure of D_{3h} symmetry

	$Cs_3Cl_2^+$			
Property	DFT B1	MP2 B1	DFT B2	MP2 B2
R_e(Cs–Cl)	3.349	3.309	3.315	3.258
α_e	92.0	92.9	90.9	91.2
h_{iso}	0.0	−15.0	−4.6	−27.7
(A_1')	149	156	148	152
(A_1')	64	68	65	63
(A_2'')	118	121	122	129
(E')	123	131	124	131
(E')	37	35	37	35
(E'')	90	99	91	100
	$Cs_2Cl_3^-$			
Property	DFT B1	MP2 B1	DFT B2	MP2 B2
R_e(Cs–Cl)	3.353	3.305	3.319	3.260
α_e	89.3	88.5	89.3	89.5
h_{iso}	−16.4	−33.6	−15.7	−39.6
(A_1')	145	145	137	144

(A_1')	65	62	65	66
(A_2'')	121	124	117	123
(E')	133	134	124	136
(E')	59	60	58	54
(E'')	89	93	80	90

R_e(Cs−Cl) is the internuclear distance, Å; α_e is the valence angle in degrees; h_{iso} is the relative energy of isomer, kJ/mol; ω_i are the frequencies of normal vibrations, cm^{-1}. The vibrational representation is $\Gamma = 2A_1' + A_2'' + 2E' + E''$

The tendency in the internuclear distances, along the sequence of the levels, holds in general for both $Cs_3Cl_2^+$ and $Cs_2Cl_3^-$ ions and for both isomers, cyclic and bipyramidal, as well. The other parameters, among which the valence angles and the vibrational frequencies, including the deformation frequencies, remain more or less constant in the series of the methods considered here.

To evaluate the outcome of the theory level on the thermodynamic functions, we computed the reduced Gibbs energy $\Phi°(T)$ of the ions in the rigid rotator–harmonic oscillator approximation using the geometrical parameters and vibrational frequencies correspondent to each theoretical approximation. The values of $\Phi°(T)$ at 1000 K are listed in Table 7. The results obtained with different methods were sufficiently close to each other in a line, so the difference in the $\Phi°(T)$ didn't exceed 5 J/(mol·K) from DFT B1 to MP2 B2. But for V-shaped $Cs_3Cl_2^+$ and linear $Cs_2Cl_3^-$ ion especially, the difference in $\Phi°(T)$ was noticeably higher. Thus for the last case, the difference between MP2 B1 and MP2 B2 results achieved 24 J/(mol·K). The primary cause of this discrepancy is the difference in deformation frequencies obtained with different methods of computation considered here (Tables 3, 4).

Table 7: Reduced Gibbs Energy, Φ^o(1000 K) in J/(mol·K), of tri- and pentaatomic ions

Ion	DFT B1	MP2 B1	DFT B2	MP2 B2
Cs_2Cl^+	354.0	355.8	356.3	353.4
$CsCl_2^-$	346.8	349.2	347.5	350.8
$Cs_3Cl_2^+$ (V-shaped)	542.1	548.3	545.7	537.8
$Cs_3Cl_2^+$ (cyclic)	516.9	514.7	520.5	515.7
$Cs_3Cl_2^+$ (bipyramidal)	485.6	482.9	484.6	482.4
$Cs_2Cl_3^-$ (linear)	541.2	561.8	559.3	537.9
$Cs_2Cl_3^-$ (cyclic)	504.0	504.4	505.4	503.1
$Cs_2Cl_3^-$ (bipyramidal)	466.5	465.3	469.9	466.4

So we came to the conclusion that if low frequencies occur in a molecule/ion, careful choice of the theoretical level and comprehensive approach are required to get the reliable values of the frequencies and hence thermodynamic functions. Nevertheless it is worth to note that the lowest approach (DFT B1) gives almost the same result as the highest one (MP2 B2).

In order to draw the final conclusion about the content of the isomers of pentaatomic ions in saturated vapor over cesium chloride, we have taken into account the entropy factor. We considered the isomerization reactions which are given below:

$Cs_3Cl_2^+$ (*V-shaped*) = $Cs_3Cl_2^+$ (*cyclic* or *bipyramidal*) (1)

$Cs_2Cl_3^-$ (*linear*) = $Cs_2Cl_3^-$ (*cyclic* or *bipyramidal*) (2)

To calculate the relative concentrations of the isomers we used the following formula

$$\Delta_r H^o(0\ \mathrm{K}) = -RT\ln(p_{iso}/p) + T\Delta_r\Phi^o(T) \quad (3)$$

where p_{iso}/p is the ratio between the pressure of the ions of the cyclic or bipyramidal isomeric form and the pressure p of V-shaped isomer for $Cs_3Cl_2^+$ or linear for $Cs_2Cl_3^-$; $\Delta_r\Phi^o(T)$ is the change in the reduced Gibbs energy of the isomerization reactions.

The enthalpies of the isomerization reactions $\Delta_r H^o(0\ \mathrm{K})$ were obtained on the base of the relative energy of isomers h_{iso} and the zero point vibration energy correction $\Delta\varepsilon$:

$$\Delta_r H^o(0\ \mathrm{K}) = h_{iso} + \Delta\varepsilon_{iso}. \quad (4)$$

The value of $\Delta\varepsilon_{iso}$ was calculated using the formula

$$\Delta\varepsilon_{iso} = 1/2hc(\Sigma\omega_{i\,prod} - \Sigma\omega_{i\,react}) \qquad (5)$$

where *h* is the Planck's constant, *c* is the speed of light in free space, $\Sigma\omega_{i\,prod}$ and $\Sigma\omega_{i\,react}$ are the sums of the vibrational frequencies of the products and reactants, respectively.

The concentration of the isomers was found of the in the temperature range between 700 and 1500 K correspondent to the mass spectrometric experiment usually. The temperature dependences of isomer concentration are shown in Fig 3. As it is seen the relative amount either of cyclic or bipyramidal isomers is not big enough and decreased when the temperature is increased. For instance, at 1000 K the largest abundance of about 13% is predicted for the cyclic isomer of $Cs_3Cl_2^+$ ion. Note, that the results shown here were obtained by using MP2 B2 method, but for the other methods, the concentration of these two isomeric forms would be even less.

Therefore the most abundant isomer in saturated vapor is the angular V-shaped isomer for $Cs_3Cl_2^+$ and linear one for $Cs_2Cl_3^-$. The low amount of the cyclic and bipyramidal isomeric forms may be explained by the prevailing effect of the entropy factor. The considerable decrease in entropy and hence in the reduced Gibbs energy $\Delta_r\Phi^o(T)$ in the isomerization reactions dominate over the energy factor and lead to a higher concentration of the angular isomer for $Cs_3Cl_2^+$ and linear one for $Cs_2Cl_3^-$.

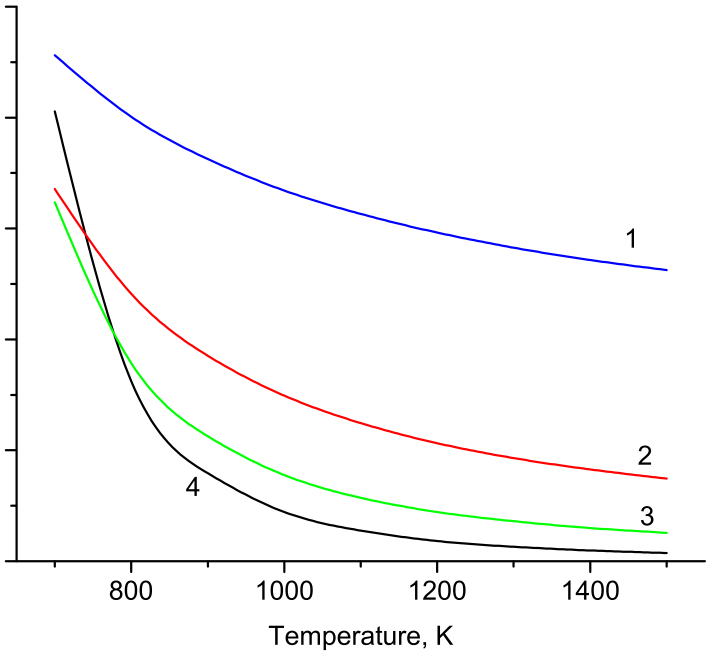


Figure 3: Relative concentration of isomers:
1 – $Cs_3Cl_2^+$(cyclic)/$Cs_3Cl_2^+$(V-shaped);
2 – $Cs_2Cl_3^-$(cyclic)/$Cs_2Cl_3^-$(linear),
3 – $Cs_3Cl_2^+$(bipyramidal)/$Cs_3Cl_2^+$(V-shaped),
4 – $Cs_2Cl_3^-$(bipyramidal)/$Cs_2Cl_3^-$(linear)

Enthalpies of ion molecular reactions and enthalpies of formation of the ions

The dissociation energies ΔE of the tri- and pentaatomic ions were calculated using the four methods, and the results are given in Table 8. For the pentaatomic ions, the values of ΔE were calculated for the most abundant isomers. Besides, the dissociation energies ΔE were calculated with MP4 B2 method which allowed us to obtain more accurate values of ΔE and the MP4 B2 results we considered as reference quantities to analyze the values of ΔE obtained by the other four methods. The comparison of the data in Table 8 shows the MP2 B2 level gives the closest fit to the reference quantity while the results obtained with the DFT B2 and MP2 B1 methods are less appropriate.

Table 8: Energies and enthalpies of the dissociation reactions and enthalpies of formation of ions (in kJ/mol)

Quantity, method	Cs_2Cl^+ = CsCl + Cs^+	$CsCl_2^-$ = CsCl + Cl^-	$Cs_3Cl_2^+$ = CsCl + Cs_2Cl^+	$Cs_2Cl_3^-$ = CsCl + $CsCl_2^-$
ΔE DFT B1	164	147	115	112
MP2 B1	171	153	121	118
DFT B2	158	145	109	106
MP2 B2	169	156	120	118
MP4 B2	167	155	119	117
ΔE_c MP4 B2	164	153	113	113
$\Delta\varepsilon$ MP2 B2	−0.9	−0.7	−0.7	−0.5
$\Delta_r H^\circ(0\ K)$ theoretical	163 ± 4	153 ± 3	112 ± 7	113 ± 5
$\Delta_r H^\circ(0\ K)$ based on experiment	153 ± 7	142 ± 7	110 ± 9	104 ±10
$\Delta_f H^\circ(0\ K)$ theoretical $\Delta_f H^\circ(0\ K)$ based on experiment	51 ± 4 61 ± 8	−622 ± 3 −611 ± 8	−301 ± 8 −289 ± 12	−975 ± 6 −955 ± 12
$\Delta_f H^\circ(0\ K)$ reference	57 ± 20	−625 ± 20	−312 ± 30	−994 ± 30

ΔE is the energy of the reaction; ΔE_c is the energy of the reaction when the BSSE correction have been taken into account; $\Delta\varepsilon$ is the zero point vibration energy correction; $\Delta_r H^\circ(0\ K)$ theoretical is the enthalpy of the reaction equal to $\Delta E_c + \Delta\varepsilon$; $\Delta_r H^\circ(0\ K)$ based on experiment was obtained by the third law of thermodynamics using the equilibrium constants from (Pogrebnoi, et al., 2002). The reference data $\Delta_f H^\circ(0\ K)$ were taken from (Gusarov, 1986).

To get more accurate energies of the dissociation reactions, the basis set superposition error (BSSE) was taken into account using the counterbalance method (Boys & Bernardi 1970). The energies of the reactions obtained with BSSE corrections are denoted as ΔE_c in Table 8. It should be emphasized that the lower level approximation DFT B1 provides us the energies of the reaction ΔE which appeared to be in an appropriate agreement with the values of ΔE_c. It may be explained by so called “compensation of errors” due to incompleteness of basis set B1 on the one hand and the limitation of DFT method on the other hand.

The enthalpies of the reactions $\Delta_r H^\circ(0\ K)$ called the “theoretical” in Table 8 were calculated using the formula

$$\Delta_r H^\circ(0\ K) = \Delta E_c + \Delta\varepsilon \qquad (6)$$

where $\Delta\varepsilon$ is the zero point vibration energy correction for the dissociation reaction.

The values of $\Delta_r H^o(0\ \mathrm{K})$ called "based on experiment" were calculated using the equilibrium constants K_p^o for the heterophase reactions from (Pogrebnoi, et al., 2002) and the procedure of the third law of thermodynamics:

$$\Delta_r H^o(0\ \mathrm{K}) = -RT\ln K_p^o + T\Delta_r\Phi^o(T). \quad (7)$$

The thermodynamic functions of atomic ions Cs^+, Cl^-, alkali metal chlorides CsCl in the condensed and in gaseous phase were taken from (Gurvich, et al., 1992-2000). The thermodynamic functions of the cluster ions Cs_2Cl^+, $CsCl_2^-$, $Cs_3Cl_2^+$, and $Cs_2Cl_3^-$ were calculated in this work using the molecular constants obtained with the MP2 B2 method. In order to convert the enthalpies of heterophase reactions into the enthalpies of gas phase reactions, we used the sublimation enthalpies of CsCl from (Gurvich, et al., 1992-2000).

The uncertainties in the theoretical enthalpies of the reactions were estimated from the comparison of MP2 B2 and MP4 B2 results. The uncertainties of the dissociation enthalpies "based on experiment" included errors in equilibrium constants (Pogrebnoi, et al., 2002), the standard deviation in the $\Delta_r H^o(0\ \mathrm{K})$ values calculated by the third law of thermodynamics, and the uncertainties in the reduced Gibbs energy.

The theoretical values of $\Delta_r H^o(0\ \mathrm{K})$ and the values "based on experiment", as seen in Table 8, agree between each other within the uncertainty limits. The enthalpy of dissociation of positive Cs_2Cl^+ ion is bigger than that of the negative $CsCl_2^-$ ion by ~10 kJ/mol. For the positive and negative pentaatomic ions, the values of $\Delta_r H^o(0\ \mathrm{K})$ are very close to each other and less than those of the triatomic ions.

Two sets of enthalpies of formation of Cs_2Cl^+, $CsCl_2^-$, $Cs_3Cl_2^+$, and $Cs_2Cl_3^-$ ions were found: from the theoretical values of $\Delta_r H^o(0\ \mathrm{K})$ and from the values "based on the experiment" (Pogrebnoi, et al., 2002). The required enthalpies of formation of Cs^+, Cl^-, and CsCl were taken from (Gurvich, et al., 1992-2000). The enthalpies of formation of these two sets agree with each other (Table 8) that confirms the reliability of the experimental and the theoretical results.

Our values of $\Delta_f H^o(0\ \mathrm{K})$ are also in accord with the available reference data. Note that the reference data from (Gusarov, 1986) were based on ionic model calculations and had rather big uncertainties. As the final results we recommend our theoretical values of enthalpies of formation of ions as the most reliable.

4. Conclusion

The properties of the cluster ions Cs_2Cl^+, $CsCl_2^-$, $Cs_3Cl_2^+$, and $Cs_2Cl_3^-$ existing in saturated vapor over CsCl were calculated. The effect of basis set and computation method on the calculated geometrical parameters, vibrational frequencies and thermodynamic characteristics was analyzed. The four theoretical approximations were considered such as DFT B1, MP2 B1, DFT B2 and MP2 B2. The values of low frequencies exposed to be quite sensitive to the applied theoretical level. All the data set about the ion properties is essential to estimate the suitability of the theoretical level. The MP2 method with the extended basis B2 set was accepted as the more accurate among the others for the calculations of the properties of the cluster ions mentioned above.

The equilibrium structure of the triatomic ions Cs_2Cl^+ and $CsCl_2^-$ is the linear of $D_{\infty h}$ symmetry. For the pentaatomic ions, three isomeric forms were considered. The most abundant isomer in saturated vapor was found the angular V-shaped of C_{2v} symmetry for $Cs_3Cl_2^+$ and the linear of $D_{\infty h}$ symmetry for $Cs_2Cl_3^-$. The other two forms, cyclic and bipyramidal, correspond to minima at the potential energy surface and have comparable or even lower energy than the first one; nevertheless, the relative amount of cyclic and bipyramidal isomers in saturated vapor is small.

The energies of dissociation of the ions were calculated using the four theoretical approximations and taking into consideration the basis superposition error. The MP2 B2 method was found as most reliable. It should be noticed also that the lower level approximation DFT B1 seems to be appropriate for calculation of thermodynamic properties of the ions because it exhibits rather good agreement with the higher level calculation. Thus it can be used when the higher level methods would not possible to be performed.

The enthalpies of the dissociation of the ions $\Delta_r H^o(0\ K)$ were found theoretically and also on the basis of available equilibrium constants of reactions. The theoretical and the "based on experiment" values of $\Delta_r H^o(0\ K)$ agree with each other within the uncertainty limits. That confirms the reliability of both the experiment and theoretical results. The enthalpies of formation of the ions were found.

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