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Chapter 21
Theoretical Study of Structure, Vibration Spectra and Thermodynamic Properties of Cluster Ions in Vapors over Potassium, Rubidium and Cesium Chlorides

Tatiana P. Pogrebnaya, Jean B. Hishamunda, Camille Girabawe, and Alexander M. Pogrebnoi

Abstract The geometrical structure, the frequencies of normal vibrations, and the thermodynamic characteristics of tri- and pentaatomic cluster ions M_2Cl^+, MCl_2^-, $M_3Cl_2^+$, and $M_2Cl_3^-$ (M = K, Rb, or Cs) existing in saturated vapors over potassium, rubidium, and cesium chlorides have been calculated by nonempirical methods. According to the calculations, the triatomic ions have a linear equilibrium configuration of $D_{\infty h}$ symmetry. For the pentaatomic ions $M_3Cl_2^+$ and $M_2Cl_3^-$, three isomeric forms were considered. The most abundant isomer in saturated vapor was found to be the linear one ($D_{\infty h}$) for $K_3Cl_2^+$, $Rb_3Cl_2^+$, $K_2Cl_3^-$, $Rb_2Cl_3^-$ and $Cs_2Cl_3^-$, and the angular V-shaped (C_{2v}) for $Cs_3Cl_2^+$. The concentration of the other two isomers, cyclic and bipyramidal, is negligible. The energies and enthalpies of dissociation of the ions have been found. The enthalpies of formation of the ions, $\Delta_f H°(0 \text{ K})$ in kJ/mol, were obtained: 116 ± 3 (K_2Cl^+), -623 ± 3 (KCl_2^-), -228 ± 7 ($K_3Cl_2^+$), -971 ± 6 ($K_2Cl_3^-$), 91 ± 3 (Rb_2Cl^+), -620 ± 3 ($RbCl_2^-$), -256 ± 5 ($Rb_3Cl_2^+$), -967 ± 4 ($Rb_2Cl_3^-$), 51 ± 4 (Cs_2Cl^+), -622 ± 3 ($CsCl_2^-$), -301 ± 8 ($Cs_3Cl_2^+$), -975 ± 6 ($Cs_2Cl_3^-$).

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21.1 Introduction

The M_2X^+, MX_2^-, $M_3X_2^+$ and $M_2X_3^-$ type ions (M is an alkali metal; X is halogen) were recorded in vapors over alkali metal halides in mass spectrometric studies [1–5]. Similar ions are of great importance in different applications: ionic implantation, ion thrusters, MHD generators, aerospace investigations, etc. Experimental data about the structure and spectra of these cluster ions are unavailable. Previously, nonempirical investigations of structure and properties had been done for the ions existing in vapors over sodium halides [6–8]. At present work, quantum chemical study has been performed for tri- and pentaatomic ions M_2Cl^+, MCl_2^-, $M_3Cl_2^+$ and $M_2Cl_3^-$ where M = K, Rb or Cs. Our aims were as follows: to determine the equilibrium geometrical structure of the ions; to compute the normal vibrational frequencies, to find out the possible isomeric configurations of the pentaatomic ions and the relative concentration in saturated vapors. Based on the molecular parameters determined in this work, together with equilibrium constants taken from high temperature mass spectrometric investigations [1–5], thermodynamic functions and thermodynamic properties of the ions were to be found.

21.2 Methodology

The calculations were performed using the GAMESS program [9] (PC GAMESS version 7.1.C [10]) implementing the following methods: electron density functional theory (DFT) with the Becke–Lee–Yang–Parr functional (B3LYP5), second order and fourth order Möller–Plesset perturbation theory (MP2 and MP4).

To choose the appropriate theory level, the calculations of properties of the diatomic alkali metal chloride molecules were performed using DFT and MP2 methods in two basis sets. The first basis set was constricted and the second was extended, we denoted them as B1 and B2 respectively. The basis set B1 was the McLean-Chandler full-electron basis set (6s5p1d) augmented with diffuse functions of the s- and p-type for Cl [9]; and the relativistic effective core potential with cc-pVTZ basis set (5s4p1d) for valence shells [11] was used for K, Rb, Cs. The extended basis set B2 was the full-electron basis set cc-pVTZ (5s4p2d1f) augmented with diffuse functions of the s, p, d, and f type for Cl [11] and the relativistic effective core potentials [11] for K, Rb, Cs. The valence shells of the metal atoms were described by correlation consistent basis sets cc-pVTZ [11]: (5s4p2d1f) on K, (7s5p4d1f) on Rb, and (6s5p4d1f) on Cs.

The optimization of the geometric parameters of the ions and the calculations of vibrational frequencies in the harmonic approximation were carried out by the methods implemented in the GAMESS program. In the calculations by MP2 and MP4 methods, the 1s, 2s, 2p orbitals of Cl were frozen.

21.3   Results and Discussion

21.3.1   Diatomic Molecules KCl, RbCl, and CsCl

The equilibrium internuclear distance, the normal vibration frequency, and the ionization potential are given in Table 21.1 for KCl, RbCl, and CsCl molecules. These calculated values are compared with the reference data.

As it is seen from Table 21.1, the results obtained with MP2 method and the extended basis set B2 are better to correspond to the reference data than the results obtained with the other three methods. Therefore we have chosen the theory level MP2 B2 for further computation of the properties of the ions. The internuclear distances calculated for KCl, RbCl, and CsCl molecules are systematically overrated about 0.03–0.06 Å and the frequencies are underrated by 2–3% compared with the experimental data. We expect the similar uncertainties in the values of R_e and ω_i for the tri- and pentaatomic ions. The results represented below for the ions correspond to the MP2 B2 calculations.

Table 21.1 Calculated and experimental parameters for KCl, RbCl and CsCl molecules

	R_e(M–Cl), Å	ω_e, cm^{-1}	μ_e, D	IP, eV
Method	KCl			
DFT B1	2.746	255	11.3	5.6
MP2 B1	2.750	257	11.7	9.0
DFT B2	2.722	268	10.5	5.7
MP2 B2	2.709	272	10.7	9.1
Experimental	2.667 [12]	280 [12]	10.2 [13]	8.3 ± 0.2 [14]
	RbCl			
DFT B1	2.889	218	11.5	5.5
MP2 B1	2.877	223	11.8	8.9
DFT B2	2.864	219	10.8	5.6
MP2 B2	2.849	225	11.1	9.0
Experimental	2.787 [12]	233 [12]	10.5 [15]	8.2 ± 0.2 [14]
	CsCl			
DFT B1	3.001	202	11.3	5.5
MP2 B1	3.001	205	11.7	8.9
DFT B2	2.954	206	10.4	5.7
MP2 B2	2.937	209	10.7	9.1
Experimental	2.906 [12]	214 [12]	10.5 [15]	8.1 ± 0.2 [14]

R_e(M–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

21.3.2   Triatomic Ions M_2Cl^+, MCl_2^- ($M = K$, Rb, or Cs)

According to the calculations, the structure of all triatomic ions is linear with $D_{\infty h}$ symmetry. The properties, namely the equilibrium internuclear distances, the total electron energies, the frequencies of normal vibrations, the intensities of vibrations in IR spectra are represented in Table 21.2.

As is seen in Table 21.2, the increase in the internuclear distances R_e(M–Cl) in series K–Rb–Cs either in positive or in the negative ions is similar to those in the MCl molecules given in Table 21.1. It is evident also that increase of the values R_e(M–Cl) correlates with the enlarging of the ionic radius in the series K^+–Rb^+–Cs^+. As concerns frequencies, the stretching symmetric vibration frequency ω_1 is smaller than the antisymmetric ω_2 in all cases. For the positive ions, the stretching vibration ω_1 may be considered to be close to the frequency ω_e in the diatomic molecules respectively. For the K_2Cl^+ and KCl_2^- ions, the frequencies are similar to each other respectively, while for the other two pairs, Rb_2Cl^+ and $RbCl_2^-$, Cs_2Cl^+ and $CsCl_2^-$, the corresponding frequencies are markedly different. In addition, the intensities of the vibrations ω_2 and ω_3 active in IR spectra are of the same magnitude approximately.

21.3.3   Pentaatomic Ions $M_3Cl_2^+$ and $M_2Cl_3^-$ ($M = K$, Rb, or Cs)

Several probable geometric configurations of the pentaatomic ions $M_3Cl_2^+$ and $M_2Cl_3^-$ (M = K, Rb, or Cs) were considered: $D_{\infty h}$ linear symmetry, C_{2v} planar cyclic symmetry, and D_{3h} bipyramidal symmetry (Fig. 21.1). For each configuration the geometric parameters were optimized, and the frequencies of normal vibrations were calculated.

The obtained parameters of the linear structure are given in Table 21.3. According to the calculations performed, the equilibrium structure of ions $K_3Cl_2^+$, $K_2Cl_3^-$, and $Rb_2Cl_3^-$ found to be linear. As concerns the other three ions, the imaginary frequencies were found: $\omega_7(\Pi_u)$ for $Rb_3Cl_2^+$, $Cs_3Cl_2^+$, and $Cs_2Cl_3^-$ and $\omega_5(\Pi_g)$ for $Cs_2Cl_3^-$.

In the case of $Rb_3Cl_2^+$ and $Cs_2Cl_3^-$, the optimization procedure showed the "slightly distorted linear" configuration of C_2 symmetry. Meanwhile, no energy decrease of this distorted configuration compared with the linear structure was observed. Note that DFT method indicated the linear structure of these two ions also. Therefore we assumed that the equilibrium structure of $Rb_3Cl_2^+$ and $Cs_2Cl_3^-$ must be linear. The imaginary deformation frequencies were substituted by the values given in Table 21.3 between the parentheses. These frequencies were estimated by the comparative method based on the tendency in frequency change in the series $K_3Cl_2^+$ – $Rb_3Cl_2^+$ – $Cs_3Cl_2^+$ and $K_2Cl_3^-$ – $Rb_2Cl_3^-$ – $Cs_2Cl_3^-$.

As to $Cs_3Cl_2^+$ ion, the optimization procedure gave the V-shaped angular structure with C_{2v} symmetry shown in Fig. 21.1. The geometric parameters

Table 21.2 Properties of the triatomic ions

Property	K_2Cl^+	Rb_2Cl^+	Cs_2Cl^+	KCl_2^-	$RbCl_2^-$	$CsCl_2^-$
$R_e(M{-}Cl)$	2.827	2.978	3.100	2.878	3.038	3.178
E	−516.08762	−507.65320	−499.77527	−947.84470	−943.62018	−939.67506
$\omega_1\ (\Sigma_g^+)$	153	98	77	155	147	143
$\omega_2\ (\Sigma_u^+)$	261	226	209	239	179	150
$\omega_3\ (\Pi_u)$	43	38	38	50	29	15
A_2	2.10	1.66	2.08	2.06	1.90	2.30
A_3	2.02	1.24	0.91	2.17	1.96	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^{2}amu^{-1}Å^{-2}
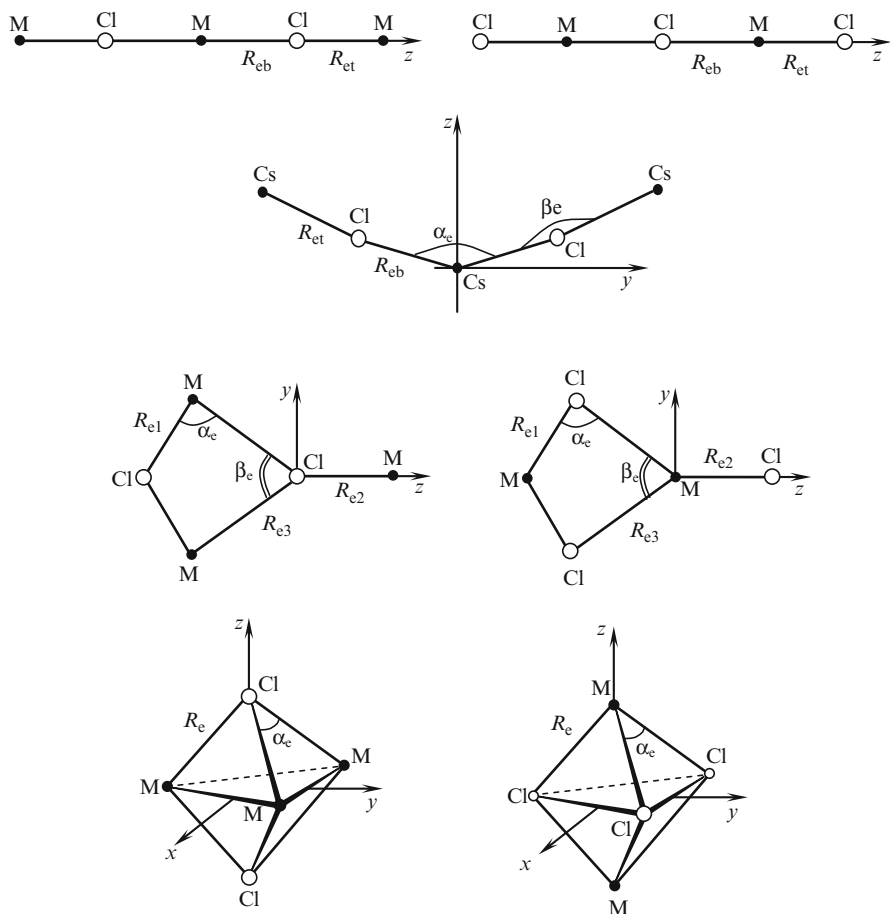
Fig. 21.1 Isomers of the pentaatomic ions: linear, angular, cyclic, and bipyramidal

and vibration frequencies are given in Table 21.4. As is seen from the data, the central fragment Cl-Cs-Cl was specified by the angle $\alpha_e = 141°$ whereas the Cs-Cl-Cs fragments were found almost linear. The energy was decreased by $h = E(C_{2v}) - E(D_{\infty h}) = -0.5$ kJ/mol. Thus among the number of considered pentaatomic ions the only one was not found to be linear but definitely bent.

The other two structures, cyclic (C_{2v}) and bipyramidal (D_{3h}), were found to be equilibrium as well. The valence angles α_e and β_e of the cyclic isomer and α_e of the bipyramidal isomers were close to 90°. The values of relative energy h_{iso} of these two types of isomers with respect to linear (or angular V-shaped for $Cs_3Cl_2^+$) are given in Table 21.5. All the ions, except the cyclic $K_3Cl_2^+$ and $K_2Cl_3^-$, have the negative value of h_{iso}. That means that the bipyramidal isomers of all ions and the cyclic isomers of $Rb_3Cl_2^+$, $Cs_3Cl_2^+$, $Rb_2Cl_3^-$, and $Cs_2Cl_3^-$ are energetically more stable than those of linear structure (or angular V-shaped for $Cs_3Cl_2^+$).

Table 21.3 Properties of the pentaatomic ions of $D_{\infty h}$ symmetry

Property	$K_3Cl_2^+$	$Rb_3Cl_2^+$	$Cs_3Cl_2^+$	$K_2Cl_3^-$	$Rb_2Cl_3^-$	$Cs_2Cl_3^-$
$R_{et}(M–Cl)$	2.793	2.941	3.051	2.833	2.988	3.117
$R_{eb}(M–Cl)$	2.910	3.074	3.228	2.927	3.096	3.256
E	−1004.13243	−991.47513	−979.65415	−1435.88960	−1427.44184	−1419.55305
$\omega_1\left(\sum_g{}^+\right)$	254	222	206	238	183	162
$\omega_2\left(\sum_g{}^+\right)$	89	61	49	88	71	53
$\omega_3\left(\sum_u{}^+\right)$	265	221	200	252	197	172
$\omega_4\left(\sum_u{}^+\right)$	176	112	84	184	171	158
$\omega_5\left(\Pi_g\right)$	32	31	27	37	18	(15)
$\omega_6\left(\Pi_u\right)$	52	38	28	53	33	23
$\omega_7\left(\Pi_u\right)$	12	(9)	10i	9	9	(9)
A_3	4.07	3.35	4.27	3.94	2.98	1.44
A_4	0.02	0.00	0.01	0.10	0.61	2.98
A_6	3.01	2.24	1.66	3.35	2.54	1.55
A_7	0.52	–	–	0.34	0.53	–

$R_{et}(M–Cl)$ and $R_{eb}(M–Cl)$ 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^{2}amu^{-1}Å^{-2}

Table 21.4 Properties of the $Cs_3Cl_2{}^+$ ion of V-shape

Property	$Cs_3Cl_2{}^+$ (C_{2v})
R_{et}(Cs–Cl)	3.052
R_{eb}(Cs–Cl)	3.213
α_e(Cl–Cs–Cl)	141.1
β_e(Cs–Cl–Cs)	179.7
E	−979.65434
$E - E(D_{\infty h})$	−0.5
ω_1 (A_1)	208
ω_2 (A_1)	56
ω_3 (A_1)	35
ω_4 (A_1)	35
ω_5 (A_1)	10
ω_6 (A_2)	86
ω_7 (A_2)	28
ω_8 (B_1)	201
ω_9 (B_1)	28
μ_e	6.1

R_{et}(M–Cl) and R_{eb}(M–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 $\Gamma = 5A_1 + 2A_2 + 2B_1$. Analysis of vibrational modes was performed using the SHRINK software [16]; the Q2SHRINK program [17] was used for building the input for SHRINK

In order to draw the final conclusion about the content of the isomers of pentaatomic ions in saturated vapor, it is necessary to take into account the entropy factor. To evaluate the relative isomer contents in saturated vapor over alkali metal chlorides, we performed thermodynamic calculations. We considered the isomerization reactions from the linear into cyclic or bipyramidal configurations:

$$M_3Cl_2{}^+ (D_{\infty h}) = M_3Cl_2{}^+ (C_{2v} \text{ or } D_{3h}) \tag{21.1}$$

$$M_2Cl_3{}^- (D_{\infty h}) = M_2Cl_3{}^- (C_{2v} \text{ or } D_{3h}) \tag{21.2}$$
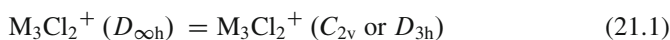
Instead of linear, the equilibrium angular V-shaped structure was considered for the $Cs_3Cl_2{}^+$. To calculate the relative concentration of the isomers we used the following formula

$$\Delta_r H°(0\,K) = RT ln(p_{iso}/p) + T\Delta_r\Phi°(T) \tag{21.3}$$

Table 21.5 Enthalpies of isomerization reactions and relative concentrations of the isomers at 1,000 K

Isomerization reaction	h_{iso}, kJ/mol	$\Delta\varepsilon$, kJ/mol	$\Delta_r H°(0\ K)$, kJ/mol	$\Delta_r \Phi°(T)$, J/(mol·K)	p_{iso}/p
$K_3Cl_2^+$ (linear) = $K_3Cl_2^+$ (cyclic)	1.8	0.8	2.6	−22.925	0.047
$K_3Cl_2^+$ (linear) = $K_3Cl_2^+$ (bipyramidal)	−16.4	1.7	−14.7	−56.593	0.007
$K_2Cl_3^-$ (linear) = $K_2Cl_3^-$ (cyclic)	2.7	0.8	3.5	−37.590	0.007
$K_2Cl_3^-$ (linear) = $K_2Cl_3^-$ (bipyramidal)	−14.2	1.6	−12.6	−70.040	0.001
$Rb_3Cl_2^+$ (linear) = $Rb_3Cl_2^+$ (cyclic)	−1.0	0.7	−0.3	−21.573	0.077
$Rb_3Cl_2^+$ (linear) = $Rb_3Cl_2^+$ (bipyramidal)	−21.1	1.6	−19.5	−55.312	0.014
$Rb_2Cl_3^-$ (linear) = $Rb_2Cl_3^-$ (cyclic)	−2.5	0.9	−1.6	−32.698	0.024
$Rb_2Cl_3^-$ (linear) = $Rb_2Cl_3^-$ (bipyramidal)	−23.4	1.5	−21.9	−67.040	0.004
$Cs_3Cl_2^+$ (angular) = $Cs_3Cl_2^+$ (cyclic)	−6.1	0.6	−5.4	−22.162	0.134
$Cs_3Cl_2^+$ (angular) = $Cs_3Cl_2^+$ (bipyramidal)	−27.7	1.1	−26.6	−55.433	0.031
$Cs_2Cl_3^-$ (linear) = $Cs_2Cl_3^-$ (cyclic)	−12.3	0.9	−11.4	−34.855	0.060
$Cs_2Cl_3^-$ (linear) = $Cs_2Cl_3^-$ (bipyramidal)	−39.5	1.5	−38.0	−71.501	0.018

h_{iso} is the relative energy of the isomer, $\Delta\varepsilon$ is zero point vibrational energy, $\Delta_r H°(0\ K)$ is the enthalpy of the reaction, $\Delta_r \Phi°(T)$ is the reduced Gibbs energy of the reaction, p_{iso}/p is relative concentration of the isomer

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

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

$$\Delta_r H^{°}(0\,K) = h_{iso} + \Delta\varepsilon. \tag{21.4}$$

The zero point vibration energy correction was calculated using the formula

$$\Delta\varepsilon = 1/2hc \left(\sum \omega_{iprod} - \sum \omega_{ireact} \right) \tag{21.5}$$

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. According to calculations this correction was small and negative, did not exceed 1.7 kJ/mol. The values of the reduced Gibbs energy were calculated in the rigid rotator–harmonic oscillator approximation using the geometrical parameters and vibration frequencies found in this work. The results of calculations are given in Table 21.5 for the temperature of 1,000 K, common in the mass spectrometric investigations of alkali metal halides.

As it was mentioned above, the relative energy h_{iso} for the majority of isomers (excluding the cyclic isomer of $K_3Cl_2^+$ and $K_2Cl_3^-$) is negative. That means that these isomers are energetically more stable than those of the linear structure (angular in the case of $Cs_3Cl_2^+$). Nevertheless, the calculations show that the relative amount of either cyclic or bipyramidal isomers in vapors is small. The largest value of $p_{iso}/p = 13.4\%$ is predicted for $Cs_3Cl_2^+$ (cyclic).

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 $\Delta_r\Phi°(T)$ in the isomerization reaction dominate over the energy factor and lead to a higher concentration of linear isomer (angular for $Cs_3Cl_2^+$). The concentration of the cyclic and bipyramidal isomers is decreased when the temperature is increased. As an example, the temperature dependence of the isomer concentration is presented for $Cs_3Cl_2^+$ and $Cs_2Cl_3^-$ in Fig. 21.2.

21.3.4 Enthalpies of Ion Molecular Reactions and Enthalpies of Formation of the Ions

The dissociation energies of ions ΔE were calculated with MP2 and MP4 methods. For pentaatomic ions the energies of the reactions were calculated for the linear isomers (angular for $Cs_3Cl_2^+$) because they dominate in the equilibrium vapor.
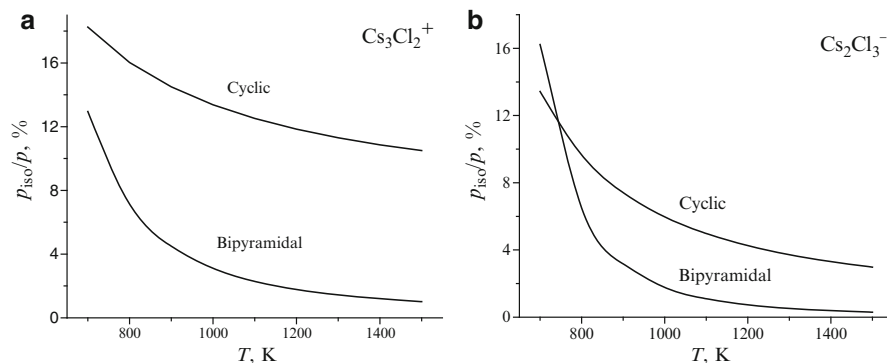
Fig. 21.2 Temperature dependence of the relative amount of the isomers of $Cs_3Cl_2^+$ (**a**) and $Cs_2Cl_3^-$ (**b**) ions

Moreover, the ion dissociation energies were calculated taking into account the basis set superposition error (BSSE) by the counterbalance method [18] using the procedure proposed by Solomonik and co-workers [19]. The energies of the reactions obtained with MP4 method and BSSE corrections are denoted as ΔE_c (Table 21.6). The BSSE correction equals to the difference of the values ΔE and ΔE_c, it was not big here but allowed us to obtain more reliable results of the dissociation energy values. The values of enthalpies of the reactions $\Delta_r H°(0\ \text{K})$ called the "theoretical" in Table 21.6 were calculated using the formula

$$\Delta_r H^{°}(0\,\text{K}) = \Delta E_c + \Delta\varepsilon \tag{21.6}$$

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

The values of $\Delta_r H°(0\ \text{K})$ called "based on experiment" were calculated using the equilibrium constants $K_p^°$ for the heterophase reactions from [3–5] and the procedure of the third law of thermodynamics:

$$\Delta_\text{r} H^{°}(0\,\text{K}) = -RT ln K_p^{°} + T\Delta_\text{r}\Phi^{°}(T). \tag{21.7}$$

The thermodynamic functions of atomic ions M^+, Cl^-, alkali metal chlorides MCl in the condensed and in gaseous phase were taken from [21]. The thermodynamic functions of the cluster ions M_2Cl^+, MCl_2^-, $M_3Cl_2^+$, and $M_2Cl_3^-$ were calculated using the molecular constants obtained in this work and listed in Tables 21.2–21.4. In order to converse the enthalpies of heterophase reactions into the enthalpies of gas phase reactions, we used the sublimation enthalpies of MCl from [21]. The enthalpies of the reactions are given in Table 21.6.

The uncertainties in the theoretical enthalpies of the reactions were estimated from the comparison of MP2 and MP4 results. The uncertainties of the dissociation enthalpies "based on experiment" included errors in equilibrium constants [3–5],

Table 21.6 Energies and Enthalpies of dissociation reactions and enthalpies of formation of ions (in kJ/mol)

Reaction	ΔE	ΔE_c	$\Delta \varepsilon$	$\Delta_r H^\circ(0)$ Theoretical	$\Delta_r H^\circ(0)$ Based on experiment	$\Delta_f H^\circ(0)$ This work	$\Delta_f H^\circ(0)$ Reference
$K_2Cl^+ = KCl + K^+$	184.0	181.8	−1.36	180 ± 3	175 ± 5	116 ± 3	113 ± 5 [1], 109 ± 10 [2]
$KCl_2^- = KCl + Cl^-$	184.8	182.5	−1.33	181 ± 3	185 ± 8	−623 ± 3	−611 ± 20 [2]
$K_3Cl_2^+ = KCl + K_2Cl^+$	139.0	131.9	−1.21	131 ± 6	128 ± 8	−228 ± 7	−263 ± 30 [2]
$K_2Cl_3^- = KCl + KCl_2^-$	139.2	135.6	−1.10	135 ± 5	120 ± 10	−971 ± 6	−1,001 ± 30 [2],
$Rb_2Cl^+ = RbCl + Rb^+$	175.7	174.1	−0.99	173 ± 3	169 ± 5	91 ± 3	94 ± 10 [2], 98 ± 5 [1]
$RbCl_2^- = RbCl + Cl^-$	171.4	170.3	−0.95	169 ± 2	No data	−620 ± 3	−624 ± 30 [2]
$Rb_3Cl_2^+ = RbCl + Rb_2Cl^+$	130.0	126.5	−0.86	126 ± 4	124 ± 8	−256 ± 5	−276 ± 30 [2]
$Rb_2Cl_3^- = RbCl + RbCl_2^-$	129.3	127.0	−0.80	126 ± 3	No data	−967 ± 4	−990 ± 30 [2]
$Cs_2Cl^+ = CsCl + Cs^+$	166.9	163.8	−0.90	163 ± 4	153 ± 7	51 ± 4	57 ± 20 [2], 36 ± 14 [20]
$CsCl_2^- = CsCl + Cl^-$	154.5	153.3	−0.68	153 ± 3	142 ± 7	−622 ± 3	−625 ± 20 [2]
$Cs_3Cl_2^+ = CsCl + Cs_2Cl^+$	118.6	112.8	−0.71	112 ± 7	110 ± 8	−301 ± 8	−312 ± 30 [2]
$Cs_2Cl_3^- = CsCl + CsCl_2^-$	116.5	113.2	−0.53	113 ± 5	104 ± 10	−975 ± 6	−994 ± 30 [2]

ΔE is the energy of the reaction, ΔE_c is the energy of the reaction when the BSSE correction has been taken into account, $\Delta \varepsilon$ is the zero point vibration energy correction, $\Delta_r H^\circ(0)$ theoretical is the enthalpy of the reaction equal to $\Delta E_c + \Delta \varepsilon$, $\Delta_r H^\circ(0)$ based on experiment was obtained by the third law of thermodynamics using the equilibrium constants from [3–5]

the standard deviation in the $\Delta_r H°(0 \text{ K})$ values calculated by the third law of thermodynamics, and the uncertainties in the reduced Gibbs energy caused by errors in frequencies which were accepted to be 10%.

The theoretical values of $\Delta_r H°(0 \text{ K})$ and the values "based on experiment", as seen in Table 21.6, agree between each other within the uncertainty limits. For the triatomic ions, the enthalpy of dissociation of positive M_2Cl^+ ions is very close to that of the negative MCl_2^- ions respectively. For the pentaatomic positive and negative ions, the values of $\Delta_r H°(0 \text{ K})$ are very close to each other also and less than those of the triatomic ions. For all ions, the decrease of the dissociation enthalpies from potassium to cesium is observed.

The enthalpies of formation of M_2Cl^+, MCl_2^-, $M_3Cl_2^+$, and $M_2Cl_3^-$ ions were calculated on the basis of the theoretical values of $\Delta_r H°(0 \text{ K})$. The required enthalpies of formation of M^+, Cl^-, and MCl were taken from [21]. Our values of $\Delta_f H°(0 \text{ K})$ of the ions are in good agreement with the available reference data (Table 21.6), but obtained with much less uncertainties.

21.4 Conclusions

The MP2 method with the extended basis set was accepted for the calculations of geometrical parameters and vibrational frequencies of the cluster ions as the more reliable method because it gives better agreement with available reference data for the diatomic molecules KCl, RbCl and CsCl.

Geometrical structure, vibrational spectra and thermodynamic properties of the ions M_2Cl^+, MCl_2^-, $M_3Cl_2^+$, and $M_2Cl_3^-$ (M = K, Rb, Cs) have been determined. The equilibrium structure of the triatomic ions M_2Cl^+ and MCl_2^- is the linear of $D_{\infty h}$ symmetry. For the pentaatomic ions $M_3Cl_2^+$ and $M_2Cl_3^-$, three isomeric forms were considered. The most abundant isomer in saturated vapor was found to be the linear one ($D_{\infty h}$) for $K_3Cl_2^+$, $Rb_3Cl_2^+$, $K_2Cl_3^-$, $Rb_2Cl_3^-$ and $Cs_2Cl_3^-$, and the angular V-shaped for $Cs_3Cl_2^+$. The other two forms, cyclic and bipyramidal, correspond to minima at the potential energy surface of the ion and have the comparable or even lower energy than the first isomer; nevertheless, according to the calculations, the relative amount of cyclic and bipyramidal isomers in saturated vapor is negligible.

The geometrical parameters and vibrational frequencies of the cluster ions vary regularly in K–Rb–Cs series.

The enthalpies of the dissociation of the ions $\Delta_r H°(0 \text{ K})$ were found by quantum chemical calculation and also on the basis of available equilibrium constants of reactions. The theoretical and the "based on experiment" values of $\Delta_r H°(0 \text{ K})$ agree between each other within the uncertainty limits. That confirms the reliability both the experiment and theoretical results.

The enthalpies of the dissociation reactions of the ions are higher for triatomic ions than those for the corresponding pentaatomic ions. The $\Delta_r H°(0 \text{ K})$ values decrease monotonically from K to Cs for both negative and positive ions. The enthalpies of formation of the ions were determined.

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