



# Molecular and ionic clusters existing in vapor over cesium chloride: Structure and thermodynamic properties



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## ARTICLE INFO

### Article history:

Received 8 August 2015  
Received in revised form 26 November 2015  
Accepted 17 December 2015  
Available online 23 December 2015

### Keywords:

Cesium chloride  
Molecular and ionic clusters  
Geometrical structure  
Vibrational spectra  
Thermodynamic properties

## ABSTRACT

The properties of neutral molecular  $\text{Cs}_2\text{Cl}_2$ ,  $\text{Cs}_3\text{Cl}_3$  and  $\text{Cs}_4\text{Cl}_4$  and the positively charged ionic clusters  $\text{Cs}_4\text{Cl}_3^+$  and  $\text{Cs}_5\text{Cl}_4^+$  existing in vapor over cesium chloride have been studied. The DFT method with B3LYP5 and B3P86 functionals, and Møller–Plesset perturbation theory of the second and fourth order have been used. The effective core potential with Def2-QZVP basis set for cesium and full electron basis set cc-pVTZ for chlorine were implemented. The geometrical parameters and vibrational frequencies of species have been determined. Isomers of two kinds have been revealed for  $\text{Cs}_3\text{Cl}_3$  and  $\text{Cs}_4\text{Cl}_3^+$  species, and their relative concentrations in vapor were evaluated. The dissociation reactions of the clusters with elimination of CsCl molecule were examined and enthalpies of reactions and enthalpies of formation of the species have been determined.

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## 1. Introduction

Cluster ions possess unique electronic, optical and magnetic properties [1–3] and serve as fundamental building blocks for new class of materials with desired properties [3,4]. Particularly cesium chloride is an essential material in manufacturing of different electronic devices. For example, CsCl thin films have been used in fabrication of silicon nanotip arrays [5,6] and micro and nano surface of silicon wafer [7] for solar cells. The CsCl ion arrays were used as a resist in reactive ion etching fabrication of certain structures on silicon surfaces [8]. Also, light emitting diodes made using self-assembled CsCl nanospheres with nano-textured indium tin oxide [9], and transparent organic light emitting devices prepared by depositing CsCl thin films [10] have been proved to enhance the output power of these devices.

The vaporization of CsCl by Knudsen effusion mass spectrometry studied by Gorokhov [11], Hilpert [12], Lisek et al. [13] where the presence of CsCl and more complicated molecules was observed. In the review by Hargittai [14] it was reported that in vapors of different alkali halides, monomers presented as the main species, while dimers, trimers and tetramers were detected in a

small amount. Similarly, the mixture of CsI,  $\text{Cs}_2\text{I}_2$  and  $\text{Cs}_3\text{I}_3$ , was detected in the vapor over CsI in [15], monomer being the main component. Furthermore, the ionic clusters of cesium chloride such as  $\text{Cs}_2\text{Cl}^+$ ,  $\text{CsCl}_2^+$ ,  $\text{Cs}_3\text{Cl}_2^+$ ,  $\text{Cs}_2\text{Cl}_3^+$ ,  $\text{Cs}_4\text{Cl}_3^+$  and  $\text{Cs}_5\text{Cl}_4^+$  had been registered in saturated vapor over cesium chloride by Knudsen effusion mass-spectrometry [16,17], and the equilibrium constants of ion-molecular reactions involving these ions had been measured.

Accurate experimental data from microwave spectroscopic measurements are available for CsCl diatomic molecule such as internuclear distance and vibrational frequency [18], ionization potential [19] and dipole moment [20]. The molecular parameters and vibrational modes of dimer, trimer and tetramer molecules as well as heptaatomic and nonatomic cluster ions are less well known. For multi-atomic inorganic species, the geometrical parameters and vibration spectra are difficult to be measured directly by experimental techniques [21]. Thus theoretical calculations play a vital role in determination of molecular structure and fundamental frequencies for the molecular and ionic clusters.

Previously quantum chemical methods were used to determine the geometrical parameters, vibration frequencies and thermodynamic properties of cluster ions existing in saturated vapors over NaX (X = F, Cl, Br, I) and MCl (M = K, Rb, Cs) [22–25]. The geometrical parameters and vibrational frequencies of tri- and pentaatomic ions of cesium chloride had been studied earlier [25,26] using quantum chemical methods, thermodynamic properties such as enthalpies of ion-molecular reaction and

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enthalpies of formation of the ions were determined. Moreover, the performance of basis sets and computational methods were examined, whereby MP2 method with extended basis set was found to be more accurate than other methods. Recently quantum chemical calculations have been performed for ionic and molecular clusters of cesium fluoride [27], bromide and iodide [28] using B3LYP5 and MP2 methods. The aim of this work is to determine geometrical structures, vibrational spectra and thermodynamic properties of  $\text{Cs}_2\text{Cl}_2$ ,  $\text{Cs}_3\text{Cl}_3$ ,  $\text{Cs}_4\text{Cl}_4$ ,  $\text{Cs}_4\text{Cl}_3^+$  and  $\text{Cs}_5\text{Cl}_4^+$  species employing the similar theoretical approaches.

## 2. Computational details

All calculations were performed using the GAMESS (US) software [29], Firefly version 8.1.0 [30], implementing the electron density functional theory (DFT) with the Becke–Lee–Yang–Parr functional (B3LYP5) [31,32] and Becke–Perdew functional (B3P86) [32–34], as well as the second and fourth order Møller–Plesset perturbation theory (MP2 and MP4). The basis sets were employed: for Cs, the effective core potential with 46 electrons in the core and Def2-QZVP basis set (6s5p4d1f) [35], and for Cl, the full-electron basis set cc-pVTZ (5s4p2d1f) augmented with *s*-, *p*-, *d*- and *f*-diffuse functions [36,37] both basis sets were accessed from EMSL (The Environmental Molecular Sciences Laboratory, US) [37,38]. The geometry of the species considered was optimized using B3LYP5, B3P86 and MP2 methods. A vibrational analysis was performed at the same level to verify that the optimized structure corresponds to a real minimum at the potential energy surface (PES) by the absence of imaginary frequencies.

The dissociation energies  $\Delta_r E$  with the elimination of CsCl molecules were calculated by all the methods B3LYP5, B3P86 and MP2. Moreover, the advanced level MP4 was employed using the optimized coordinates determined by MP2 method. The correction for basis set superposition error (BSSE) [39] has been taken into account for MP2 and MP4 using the procedure proposed in [40]. The calculations with BSSE corrections are denoted as MP2C and MP4C.

## 3. Results and discussion

### 3.1. Dimer $\text{Cs}_2\text{Cl}_2$ : structure, vibrational spectrum and enthalpy of dissociation

Different geometrical structures of the  $\text{Cs}_2\text{Cl}_2$  molecule were considered such as linear ( $C_{\infty v}$ ), planar cycle or rhomb ( $D_{2h}$ ) and non-planar cycle ( $C_{2v}$ ). Among these only rhomb with  $D_{2h}$  symmetry was found to be equilibrium. This result is similar to other presented on light alkali metal halides [14,41]. The computed and literature data of geometrical parameters, vibrational frequencies and enthalpy of dissociation reactions of the  $\text{Cs}_2\text{Cl}_2$  molecule are compiled in Table 1. The internuclear distance  $R_e(\text{Cs}-\text{Cl})$  obtained by B3P86 and MP2 methods are in better agreement with literature data, than B3LYP5 result. The fundamental frequencies computed by three methods do not contradict to each other and literature data as well.

The energy of dissociation reaction  $\Delta_r E$  of  $\text{Cs}_2\text{Cl}_2$  into two monomers has been calculated using these three methods, moreover BSSE correction has been taken into account in MP2 and MP4 calculations; thus six methods have been applied: B3LYP5, B3P86, MP2, MP2C, MP4, and MP4C. The enthalpies of reactions  $\Delta_r H^\circ(0)$  are calculated using the dissociation energies  $\Delta_r E$ , and the zero-point vibration energy (ZPVE) correction  $\Delta_r \varepsilon$  by the following equations:

$$\Delta_r H^\circ(0) = \Delta_r E + \Delta_r \varepsilon \quad (1)$$

**Table 1**  
Properties of the neutral molecule  $\text{Cs}_2\text{Cl}_2$ .

Property <sup>a</sup>	B3LYP5	B3P86	MP2	Literature data <sup>b</sup>
$R_e(\text{Cs}-\text{Cl})$	3.198	3.162	3.155	3.140 [43] 3.149 [14]
$\alpha_e(\text{Cl}-\text{Cs}-\text{Cl})$	87.9	87.8	86.7	87.0 [43] 85.6 [14]
$-E$	960.831080	961.036916	959.816057	
$\omega_1 (A_g)$	147	154	150	149 [43]
$\omega_2 (A_g)$	53	53	53	51 [43]
$\omega_3 (B_{1g})$	124	127	133	130 [43]
$\omega_4 (B_{1u})$	45	45	44	41 [43]
$\omega_5 (B_{2u})$	143	146	146	145 [43]
$\omega_6 (B_{3u})$	152	155	159	156 [43]
$I_4$	0.74	0.72	0.77	
$I_5$	1.68	1.68	1.67	
$I_6$	1.83	1.86	1.88	
$\Delta_r H^\circ(0)$	140.5	142.7	165	160.9 [42]

<sup>a</sup> Here and hereafter in Tables 2–5,  $R_e(\text{Cs}-\text{Cl})$  is the equilibrium internuclear distance, Å;  $\alpha_e(\text{Cl}-\text{Cs}-\text{Cl})$  is the valence angle, degrees;  $E$  is the total electron energy, au;  $\omega_i$  are the fundamental frequencies,  $\text{cm}^{-1}$ ;  $I_i$  are the IR intensities,  $\text{D}^2 \text{amu}^{-1} \text{Å}^{-2}$ , and  $\Delta_r H^\circ(0)$  is the enthalpy of the dissociation reaction  $\text{Cs}_2\text{Cl}_2 = 2\text{CsCl}$ ,  $\text{kJ mol}^{-1}$ . Besides the values of  $\Delta_r H^\circ(0)$  presented, the enthalpy of the reaction has been also calculated by MP4C method and equal to  $155 \pm 6 \text{ kJ mol}^{-1}$ .

<sup>b</sup> The literature data on geometrical parameters and fundamental frequencies were computed in [14,43] using MP2 method.

$$\Delta_r \varepsilon = \frac{1}{2} hc \left( \sum \omega_{i \text{ prod}} - \sum \omega_{i \text{ react}} \right) \quad (2)$$

where  $h$  is the Plank's constant,  $c$  is the speed of light in the free space,  $\sum \omega_{i \text{ prod}}$  and  $\sum \omega_{i \text{ react}}$  are the sums of the vibrational frequencies of the products and reactants, respectively. The enthalpies of the reaction calculated by all theoretical levels were compared with the reference magnitude  $\Delta_r H^\circ(0) = 160.9 \text{ kJ mol}^{-1}$  accessed from IVTANTHERMO database [42]. The theoretical values of enthalpy of dissociation reaction versus the level of calculations are shown in Fig. 1 and the reference value [42] is taken as a benchmark. It can be seen that the results obtained by B3LYP5 and B3P86 methods are underrated essentially (by  $\sim 20 \text{ kJ mol}^{-1}$ ) compared with the reference datum, while the results by MP2, MP2C, MP4 and MP4C agree much better with the reference value. Our highest level of computation MP4C gives the magnitude of  $155 \text{ kJ mol}^{-1}$  which deviates by  $\Delta = 6 \text{ kJ mol}^{-1}$  from the benchmark; this difference was accepted as the uncertainty of the result presented in Table 1.

Concluding this section about dimer molecule, all three methods B3LYP5, B3P86 and MP2 give in general reasonable results on geometrical parameters and vibrational frequencies. For the enthalpy of dissociation reaction, the results by B3LYP5 and B3P86 methods deviate much from the reference value, whereas MP2C and MP4 magnitudes agree well with the benchmark. For the heavier molecular and ionic clusters, the geometrical parameters and vibrational frequencies presented are found by B3P86 method, while MP2 and MP4 methods have been used in the computation of the energies of the dissociation reactions.

### 3.2. Trimer $\text{Cs}_3\text{Cl}_3$ and tetramer $\text{Cs}_4\text{Cl}_4$ : structure and vibrational spectra

Several alternative geometrical configurations of the trimer and tetramer were investigated. For  $\text{Cs}_3\text{Cl}_3$  molecule, three structures were considered: planar hexagonal ( $D_{3h}$ ), hexagonal non-planar ( $C_{3v}$ ), and prismatic ( $C_s$ ). The geometry of these structures was optimized; and through optimization the hexagonal non-planar one converged into planar while prismatic converged into butterfly-shaped structure. Thus for the  $\text{Cs}_3\text{Cl}_3$  molecule two isomers were confirmed to exist: planar hexagonal and

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