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THEORETICAL & COMPUTATIONAL CHEMISTRY | RESEARCH ARTICLE

Molecular clusters Cs_3X_3 and Cs_4X_4 ($X = Br, I$): Quantum chemical study of structure and thermodynamic properties

Stanley F. Mwanga^{1*}, Tatiana P. Pogrebnya¹ and Alexander M. Pogrebnoi¹

Abstract: The properties of trimer Cs_3X_3 and tetramer Cs_4X_4 ($X = Br, I$) molecules have been studied using DFT with B3LYP5 functional and MP2 and MP4 methods. Two equilibrium geometrical structures of trimers, hexagonal (D_{3h}) and “butterfly-shaped” (C_s), and one for tetramers, distorted cubic (T_d), are confirmed to exist; geometrical parameters and vibrational spectra are determined. The relative concentration of Cs_3X_3 isomers has been evaluated; the butterfly-shaped isomer dominates over hexagonal in saturated vapour in a broad temperature range. The dissociation reactions through different channels have been considered and enthalpies of formation $\Delta_f H^\circ(0)$ of clusters determined: $-858 \pm 20 \text{ kJ mol}^{-1}$ (Cs_3Br_3), $-698 \pm 20 \text{ kJ mol}^{-1}$ (Cs_3I_3), $-1270 \pm 30 \text{ kJ mol}^{-1}$ (Cs_4Br_4) and $-1045 \pm 30 \text{ kJ mol}^{-1}$ (Cs_4I_4). The Gibbs free energies $\Delta_f G^\circ(T)$ calculated for the dissociation reactions of trimer and tetramer molecules have indicated that these molecules are resistive in narrow temperature range only and decompose spontaneously with temperature increase with elimination of dimer molecules.

Subjects: Materials Science; Nanoscience & Nanotechnology; Physics

Keywords: DFT; MP2; MP4; molecular cluster; isomer; relative concentration; enthalpy of dissociation reaction and enthalpy of formation

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Alexander Pogrebnoi is a professor and lecturer; his research interests include material science, thermodynamics, high temperature mass spectrometry and quantum chemistry. The group is focused on quantum chemical study of inorganic and organic molecular and ionic clusters relating to fundamental research and practical applications in different areas. We investigate structure, vibrational and electronic spectra, thermodynamic properties of the species and energetics of chemical reactions.

PUBLIC INTEREST STATEMENT

Despite the seeming simplicity of alkali halide compounds, the composition of vapour over their solid or liquid surfaces appeared to be rather complex. Various molecular and ionic clusters were detected using mass spectrometric technique. The structure and properties of the clusters are not comprehended entirely by now. Quantum chemistry being a powerful instrument provides valuable knowledge about structure, spectra and thermodynamic properties of the species. In this work, we studied the trimer and tetramer clusters of caesium halides using the quantum chemical methods. Besides the structural properties of the species their thermodynamic stability regarding different decomposition routes is analysed. These results may be useful in industrial applications, e.g. in halogen metallurgy, manufacture of modern electronic devices, halogen lamps, chemical vapour transport and deposition.



Tatiana P. Pogrebnya

1. Introduction

The study of alkali halide clusters, ionic and molecular, has been the subject of research over past five decades. This involves both experimental (Butman, Kudin, Smirnov, & Munir, 2000; Chupka, 1959; Dunaev, Kudin, Butman, & Motalov, 2013; Gusarov, 1986; Pogrebnoi, Kudin, & Kuznetsov, 2000; Sidorova, Gusarov, & Gorokhov, 1979; Snelson, 1967) and theoretical (Cohen & Gordon, 1975; Rupp & Ahlrichs, 1977; Weis, Ochsenfeld, Ahlrichs, & Kappes, 1992; Welch, Lazareth, Dienes, & Hatcher, 1976) studies. Most experimental studies have dealt with the identification of cluster species existing in saturated vapour and measurement of equilibrium constants of ion molecular reactions. On the other hand theoretical studies concern mainly prediction of equilibrium configurations, geometrical parameters, binding energies and vibrational frequencies. These clusters are of interest because they have unique electronic, optical and magnetic properties which make them to be useful in different applications. For example, caesium chloride thin films were used in fabrication of electronic devices through ion implantation techniques (Lee, Han, Choi, & Moon, 2010; Liao, Liu, Wang, & Yi, 2011; Liu, Ashmkan, Dong, Wang, & Yi, 2013; Liu, Ferguson, Yavuz, & Cui, 2012; Zhang, Liu, Wang, Zhang, & Yi, 2014; Zhang et al., 2012). Cluster ions have been proved to be useful in ionic thrusters (Benson & Patterson, 2009) and magneto-hydrodynamic generators (Kay, 2011). Besides, caesium and iodine exist among the fission products that may be released in nuclear power plants (Badawi, Xerri, Canneaux, Cantrel, & Louis, 2012; Lennart & Kjell, 1994; Povinec et al., 2013; Roki, Ohnet, Fillet, Chatillon, & Nuta, 2013, 2014); these by-products are highly radioactive materials. Thus, evaluations of thermodynamic properties of gaseous species are essential for safety features of a nuclear pressurized reactor. The thermodynamic functions of gaseous species are usually derived by statistical thermodynamics from the geometrical parameters and vibrational frequencies.

Recently, we have theoretically investigated the properties of molecular and ionic clusters of caesium fluoride (Mwanga, Pogrebnyaya, & Pogrebnoi, 2015a), caesium chloride (Hishamunda, Girabawe, Pogrebnyaya, & Pogrebnoi, 2012; Pogrebnyaya, Hishamunda, Girabawe, & Pogrebnoi, 2012) and caesium bromide and iodide (Mwanga, Pogrebnyaya, & Pogrebnoi, 2015b). In these works, the equilibrium geometrical structure, vibrational spectra and thermodynamic properties of the clusters were determined. The dimers and trimers of caesium bromine and iodine have been studied theoretically and experimentally by Groen and Kovács (2010). Molecular clusters of lithium iodide have been found to exist in vapour over solid lithium iodide (Bencze, Lesar, & Popovic, 1998). However, tetramers of caesium bromide and iodine have not yet studied. We also anticipate that isomeric forms would exist for trimers of caesium bromine and iodine as it was revealed for caesium fluoride and chloride (Mwanga et al., 2015a; Mwanga, Pogrebnyaya, & Pogrebnoi, 2016). In this work, we present quantum chemical investigation of the properties of trimer Cs_3X_3 and tetramer Cs_4X_4 ($X = Br, I$) molecules.

2. Computational details

Quantum chemical calculations are performed using General Atomic and Molecular Electronic Structure System (GAMESS) (Schmidt et al., 1993) software package, Firefly version 8.1.0 (Granovsky, 2012). Electron density functional theory (DFT) with the Becke–Lee–Yang–Parr functional (B3LYP5) (Becke, 1993; Lee, Yang, & Parr, 1988) and second and fourth order Møller–Plesset perturbation theory (MP2 and MP4) have been used. The relativistic effective core potential ECP GEN 46 3 with basis set Def2-QZVP 6s5p4d1f for caesium (Leininger et al., 1996) is used. For bromine and iodine atoms, relativistic ECP GEN 28 4, 7 electrons in the core (Br) and ECP GEN 46 4, 7 electrons in the core (I) with SDB-aug-cc-pVTZ basis sets 4s4p3d2f (Martin & Sundermann, 2001) have been applied. These basis sets were accessed from EMSL (Schuchardt et al., 2007). The geometry of the species was optimized by B3LYP5 and MP2 methods. We expect that including the diffused functions into valence basis sets of halogen atoms, Br and I, will improve an accuracy of the calculated thermochemical properties of the species as it is based on results by Martin and Sundermann (2001) and our experience as well (Mwanga et al., 2015a). A vibrational analysis was performed at the same level of calculations to examine whether the obtained structure corresponds to a real energy minimum by the absence of the imaginary frequencies. The visualization of geometrical structure and vibrational spectra the software have been used: MacMolPlt (Bode & Gordon, 1998) and Chemcraft (“Chemcraft. Version 1.7 (build 132). G. A. Zhurko, D. A. Zhurko. HTML” (Zhurko & Zhurko, 2014).

The enthalpies of the chemical reactions $\Delta_r H^\circ(0)$ were calculated on the basis of energies $\Delta_r E$, and the zero-point vibration energy (ZPVE) correction $\Delta_r \varepsilon$ as given in following equations:

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

$$\Delta_r \varepsilon = \frac{1}{2} hc \left(\sum \omega_{iprod} - \sum \omega_{ireact} \right) \quad (2)$$

where h is the Planck constant, c is the speed of light in the free space, $\sum \omega_{iprod}$ and $\sum \omega_{ireact}$ are the sums of the vibrational frequencies of the products and reactants, respectively. This approach is similar to that applied by Curtiss, Redfern, and Frurip (2000).

The dissociation energies $\Delta_r E$ of the species were calculated by B3LYP5 and MP2 methods, MP4 was employed using the optimized coordinates determined by MP2 method. The correction for basis set superposition error (BSSE) (Boys & Bernardi, 1970) has been employed for MP2 and MP4 as well using procedure proposed by Solomonik and co-workers (Solomonik, Smirnov, & Mileev, 2005). In the DFT calculations, BSSE correction was not considered. According to Liu, Zhao, Li, and Chen (2013) as well as our previous work (Mwanga et al., 2015a), the DFT methods are not much sensitive to the BSSE correction and the latter does not improve the DFT results on energies and enthalpies of dissociation reactions.

3. Results and discussion

3.1. Trimer Cs_3Br_3 and Cs_3I_3 molecules

For trimer Cs_3X_3 molecules, two equilibrium structures were confirmed to have minima at the potential energy surface (PES): hexagonal planar (D_{3h}) and butterfly-shaped (C_s) (Figure 1(a and b)). The geometrical parameters and vibrational spectra of these structures are compiled in Tables 1 and 2. As expected, there is a progressive increase in internuclear separation from bromide to iodide. Regarding the energy, butterfly-shaped isomer possesses lower energy by ~ 14 kJ mol $^{-1}$ (Cs_3Br_3) and ~ 15 kJ mol $^{-1}$ (Cs_3I_3) than hexagonal (MP2). Thus, butterfly-shaped structure is more energetically stable than hexagonal. Similar isomeric forms were confirmed to exist for Cs_3F_3 and Cs_3Cl_3 in our previous works (Mwanga et al., 2015a, 2016), respectively. We have evaluated the energy barrier in the path from the C_s ("butterfly") to D_{3h} (hexagonal) configuration. In the molecule within C_s symmetry, the separation between two opposite atoms, Cs_2-X_2 (Figure 1(b)), was a variable parameter (transition reaction coordinate). This parameter was varied with a step of 0.5 Å from the distance in the C_s structure up to that in the hexagonal one. All other atom coordinates were optimized at each step. It was revealed that the barrier for the transition was ~ 6 kJ mol $^{-1}$ both for Cs_3Br_3 and Cs_3I_3 (DFT/B3LYP5). Heat energy of the molecules at ~ 350 K is ~ 3 kJ mol $^{-1}$, which is twice less compared to the barrier. The barrier also is much higher regarding vibrational energy quantum, that is ~ 1 kJ mol $^{-1}$.

The vibrational frequencies determined by B3LYP5 and MP2 methods are given in Tables 1 and 2. In most cases, a good agreement is observed between the corresponding frequencies found by two methods. Based on our previous experience (Mwanga et al., 2015a, 2015b, 2016) we consider that MP2 results to be more applicable for further consideration and calculation of the thermodynamic

Figure 1. Geometrical structures of the trimer Cs_3X_3 and tetramer Cs_4X_4 ($X = Br, I$) molecules: (a) Cs_3X_3 , planar hexagonal D_{3h} ; (b) Cs_3X_3 , butterfly-shaped C_s ; (c) Cs_4X_4 , distorted cube T_d .

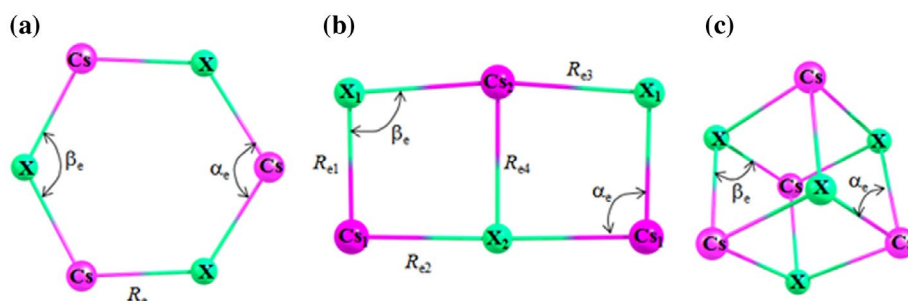


Table 1. Properties of neutral molecules Cs_3X_3 (hexagonal, D_{3h}), X = Br, I

Property	$\text{Cs}_3\text{Br}_3 (D_{3h})$		$\text{Cs}_3\text{I}_3 (D_{3h})$	
	B3LYP5	MP2	B3LYP5	MP2
$R_e(\text{Cs-X})$	3.377	3.348	3.626	3.589
$\alpha_e(\text{X-Cs-X})$	119.3	117.9	123.2	121.8
$\beta_e(\text{Cs-X-Cs})$	120.7	122.1	116.8	118.2
$-E$	100.84946	100.43294	94.95303	94.49097
$\omega_1 (A_1')$	103 (0)	114 (0)	86 (0)	91 (0)
$\omega_2 (A_1')$	68 (0)	86 (0)	58 (0)	59 (0)
$\omega_3 (A_1')$	33 (0)	43 (0)	28 (0)	28 (0)
$\omega_4 (A_2'')$	26 (0.61)	26 (0.63)	22 (0.44)	23 (0.46)
$\omega_5 (E')$	110 (1.22)	118 (1.1)	88 (0.97)	91 (0.95)
$\omega_6 (E')$	85 (0.28)	91 (0.06)	71 (0.01)	73 (0.00)
$\omega_7 (E')$	19 (0.24)	12 (0.22)	12 (0.09)	12 (0.08)
$\omega_8 (E'')$	12 (0)	12 (0)	11 (0)	11 (0)
$q(\text{Cs})$	0.834	0.881	0.800	0.860
$q(\text{X})$	-0.834	-0.881	-0.800	-0.860

Notes: Here and hereafter $R_e(\text{Cs-X})$ is the equilibrium internuclear distance, Å; $\alpha_e(\text{X-Cs-X})$ and $\beta_e(\text{Cs-X-Cs})$ are valence angles, degs; E is the total electron energy, au; ω_i are vibrational frequencies, cm^{-1} ; the values given in parentheses near the frequencies are IR intensities, $\text{D}^2 \text{amu}^{-1} \text{Å}^{-2}$.

functions of the species. The decrease in the corresponding values of ω_i is observed from bromide to iodide. Several low frequencies of $\sim 30 \text{ cm}^{-1}$ and less are found in spectra of both isomers of Cs_3X_3 : there are $\omega_3, \omega_4, \omega_7, \omega_8$ for hexagonal isomer and $\omega_5, \omega_6, \omega_7, \omega_{11}, \omega_{12}$ for C_s isomer. The assignments of vibrational frequencies for Cs_3X_3 are presented in Figures 2 and 3. As for hexagonal planar Cs_3X_3 , both species have few modes active in IR spectra, Cs-X stretching being the highest intensity. The bands of medium intensity are wagging X-Cs-X modes with low frequencies, 26 cm^{-1} (Cs_3Br_3) and 23 cm^{-1} (Cs_3I_3). The bands of weak intensity are related to rocking Cs-X-Cs vibrations with low vibration frequency of 12 cm^{-1} . Our computed vibrational spectra for $\text{Cs}_3\text{X}_3 (D_{3h})$ can be compared with experimental data in Groen and Kovács (2010) where FT-IR spectra of $(\text{CsBr})_n$ and $(\text{CsI})_n$ ($n = 1-3$) had been measured using matrix isolation technique. For the trimers, the vibrational modes 110.2 cm^{-1} in Kr and 103.1 cm^{-1} in Xe matrix for Cs_3Br_3 and 86.6 cm^{-1} in Xe for Cs_3I_3 had been recorded. Therefore our values, 118 cm^{-1} (Cs_3Br_3) and 91 cm^{-1} (Cs_3I_3), agree well with the experimental frequencies. Worth to note also that our results for the trimer molecules are in a good agreement with theoretical data (Groen & Kovács, 2010).

For butterfly-shaped isomers, the majority of vibrational modes are active in IR spectra although most of them have weak intensity. The bands of highest intensity correspond to Cs-X stretching vibrations; the most intensive bands are observed at 118 cm^{-1} (Cs-Br) and 93 cm^{-1} (Cs-I). Other valence vibrations at 67 cm^{-1} (Cs_3Br_3) and 63 cm^{-1} (Cs_3I_3) possess low intensities. The bending vibrational modes are characterized by weak intensities.

To consider the electron density distribution, we have calculated the Mulliken atomic charges q by both methods, DFT and MP2 (Tables 1 and 2). One can see the high ionicity of the species as the charges on atoms are about 0.8–0.9 au. For both isomers of Cs_3Br_3 and Cs_3I_3 , the MP2 method demonstrates higher ionicity as the charge magnitudes are bigger by 0.03–0.07 au than the corresponding values of q obtained by DFT. It is worth to mention here the dipole moments μ_e as they relate to the electron density distribution (Table 2). The values of μ_e also demonstrate that the DFT method underrates the ionic character of bonds as $\mu_e(\text{DFT}) < \mu_e(\text{MP2})$. It is evident that this correlation holds due to charges relationship, $q(\text{DFT}) < q(\text{MP2})$. On comparing two isomers, in the hexagonal one of

Table 2. Properties of neutral molecules Cs_3X_3 (“butterfly-shaped”, C_s), $X = Br, I$

Property	Cs_3Br_3 (C_s)		Cs_3I_3 (C_s)	
	B3LYP5	MP2	B3LYP5	MP2
$R_{e1}(Cs_1-X_1)$	3.303	3.264	3.553	3.517
$R_{e2}(Cs_1-X_2)$	3.429	3.374	3.680	3.615
$R_{e3}(Cs_2-X_1)$	3.487	3.431	3.734	3.674
$R_{e4}(Cs_2-X_2)$	3.737	3.606	3.986	3.842
$\alpha_e(X_1-Cs_1-X_2)$	94.0	92.0	96.5	94.3
$\beta_e(Cs_1-X_1-Cs_2)$	93.2	93.7	90.2	90.8
$\chi_e(Cs_1-X_2-Cs_2-X_1)$	169.0	169.8	172.0	173.1
$-E$	100.85067	100.43813	94.95448	94.49674
$\Delta_r E_{iso}$	-3.19	-13.63	-3.82	-15.15
ω_1 (A')	109 (1.05)	118 (1.01)	85 (1.00)	93 (0.72)
ω_2 (A')	90 (0.34)	101 (0.36)	75 (0.12)	86 (0.08)
ω_3 (A')	62 (0.10)	67 (0.14)	53 (0.06)	59 (0.07)
ω_4 (A')	44 (0.12)	61 (0.12)	39 (0.11)	50 (0.08)
ω_5 (A')	35 (0.03)	37 (0.23)	27 (0.08)	30 (0.08)
ω_6 (A')	29 (0.29)	31 (0.26)	24 (0.24)	26 (0.30)
ω_7 (A')	5 (0.01)	10 (0.01)	6 (0.00)	7 (0.01)
ω_8 (A'')	112 (0.60)	120 (0.75)	89 (0.77)	95 (0.79)
ω_9 (A'')	104 (0.62)	110 (0.41)	88 (0.00)	93 (0.21)
ω_{10} (A'')	79 (0.02)	86 (0.01)	56 (0.02)	63 (0.03)
ω_{11} (A'')	34 (0.10)	36 (0.10)	27 (0.13)	28 (0.08)
ω_{12} (A'')	16 (0.00)	16 (0.00)	13 (0.00)	13 (0.00)
μ_e	9.92	10.45	10.68	11.31
$q(Cs_1)$	0.814	0.868	0.776	0.851
$q(X_1)$	-0.834	-0.882	-0.778	-0.853
$q(Cs_2)$	0.850	0.880	0.776	0.837
$q(X_2)$	-0.811	-0.852	-0.772	-0.833

Note: $\chi_e(Cs_1-X_2-Cs_2-X_1)$ is the dihedral angle, degs; $\Delta_r E_{iso} = E(Cs_3X_3, C_s) - E(Cs_3X_3, D_{3h})$ is isomerization energy, kJ mol^{-1} ; μ_e is the dipole moment, D.

Cs_3X_3 the absolute values of charges on X and Cs atoms are equal which follows from the high symmetry of the structure. In the isomers of C_s configuration, the electron density distribution is not uniform: according to MP2 results, the side caesium atoms, Cs_1 , have slightly smaller charges (by 0.01 au) than the middle Cs_2 atom, while the side halogen atoms X_1 have bigger charge magnitudes (by ~ 0.02 au) compared to the middle one X_2 , that holds for both Cs_3Br_3 and Cs_3I_3 clusters. Ionicity slightly decreases, by 0.01–0.02 au, from the hexagonal to “butterfly” configuration and from bromide to iodide.

The relative concentration p_{II}/p_I of the isomers in the saturated vapour was evaluated using the following formula:

$$\Delta_r H^\circ(0) = T \Delta_r \Phi^\circ(T) - RT \ln \left(\frac{p_{II}}{p_I} \right) \quad (3)$$

where $\Delta_r H^\circ(0)$ is the enthalpy of the isomerization reaction $Cs_3X_3 (D_{3h}) \rightarrow Cs_3X_3 (C_s)$; T is absolute temperature; p_I is the partial pressure of the D_{3h} isomer, and p_{II} is that of C_s one; $\Delta_r \Phi^\circ(T)$ is the reduced Gibbs energy of the reaction, $\Delta_r \Phi^\circ(T) = \Phi^\circ(T)_{\text{prod}} - \Phi^\circ(T)_{\text{react}}$. The value of $\Phi^\circ(T)$ comprises the enthalpy

Figure 2. IR spectrum of planar hexagonal isomer Cs_3X_3 (D_{3h}): (a) Cs_3Br_3 and (b) Cs_3I_3 .

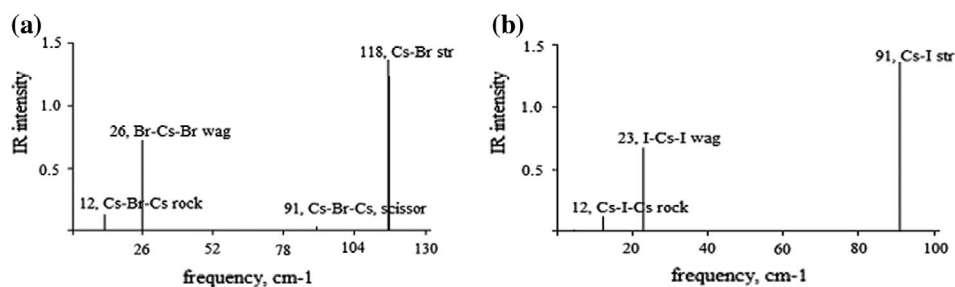
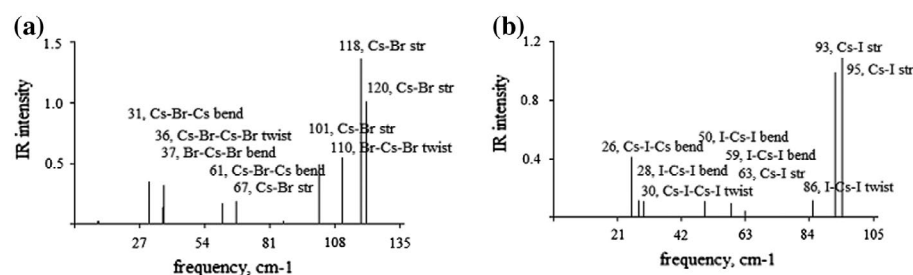


Figure 3. IR spectrum of butterfly-shaped isomer Cs_3X_3 (C_s): (a) Cs_3Br_3 and (b) Cs_3I_3 .



increment $[H^\circ(T) - H^\circ(0)]$ and entropy $S^\circ(T)$ of each species: $\Phi^\circ(T) = -[H^\circ(T) - H^\circ(0) - TS^\circ(T)]/T$. The values of $\Phi^\circ(T)$ and other thermodynamic functions were calculated using OpenThermo software (Tokarev, 2007–2009) within the “rigid rotator-harmonic oscillator” approximation; the optimized coordinates and vibrational frequencies obtained by MP2 method were used as the input parameters. The enthalpies of the isomerization reactions $\Delta_f H^\circ(0)$ were calculated on the basis of isomerization energies $\Delta_f E_{iso}$ using Equations (1 and 2). The isomerization energies $\Delta_f E_{iso}$, ZPVEs $\Delta_f \epsilon$, enthalpies $\Delta_f H^\circ(0)$ of isomerization reactions, change in the reduced Gibbs energies $\Delta_f \Phi^\circ(T)$, and the relative abundance p_{II}/p_I of the isomers at $T = 500$ K are presented in Table 3. The value of p_{II}/p_I indicates which of the isomers prevails in saturated vapour. For both species, the butterfly-shaped Cs_3X_3 (C_s) dominates over hexagonal-shaped Cs_3X_3 (D_{3h}) isomer, as the ratio p_{II}/p_I is greater than one.

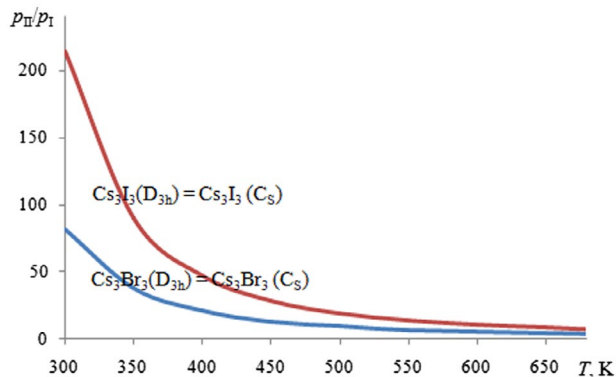
The temperature effect on the relative abundance p_{II}/p_I of the isomers is considered for temperature range between 300 and 700 K (Figure 4). As is seen, the relative concentration of the butterfly-shaped isomer at 300 K is ~ 80 for Cs_3Br_3 and ~ 200 for Cs_3I_3 , and decreases with temperature rise being still greater than one. Worth to note that the relative abundance of isomers is influenced by two factors, the isomerization energy and entropy S° of species: the lower is the $\Delta_f E_{iso}$, and bigger S° of the isomer II, the higher is the ratio p_{II}/p_I . Thus, being favoured by both of these factors, the isomer with C_s symmetry is predicted to dominate in vapour in a broad temperature range.

The enthalpies of dissociation reactions $\Delta_f H^\circ(0)$ with the elimination of CsX molecules and enthalpies of formation $\Delta_f H^\circ(0)$ of Cs_3X_3 were calculated for the C_s isomer based on MP4C results. The values of $\Delta_f H^\circ(0)$ for CsX and Cs_2X_2 molecules were taken from (Gurvich et al., 2000). The theoretical values of $\Delta_f H^\circ(0)$ were calculated using Equations (1 and 2).

Table 3. The energies $\Delta_f E_{iso}$ and enthalpies $\Delta_f H^\circ(0)$ of the isomerization reactions, change in the reduced Gibbs free energies $\Delta_f \Phi^\circ(T)$, ZPVE corrections $\Delta_f \epsilon$ and relative abundances p_{II}/p_I of the isomers ($T = 500$ K)

Isomerization reaction	$\Delta_f E_{iso}$, kJ mol ⁻¹	$\Delta_f \epsilon$, kJ mol ⁻¹	$\Delta_f H^\circ(0)$, kJ mol ⁻¹	$\Delta_f \Phi^\circ(T)$, J mol ⁻¹ K ⁻¹	p_{II}/p_I
Cs_3Br_3 (D_{3h}) = Cs_3Br_3 (C_s)	-13.63	0.35	-13.28	-8.118	9.2
Cs_3I_3 (D_{3h}) = Cs_3I_3 (C_s)	-15.15	0.41	-14.74	-5.032	18.9

Figure 4. Temperature dependence of the relative concentration of the isomers for trimers Cs_3X_3 ($X = Br, I$) molecules.



It is worth to note that the spin-orbit coupling effect may be important for heavy atoms, especially for species with two or more low lying electronic states (Fedorov, Koseki, Schmidt, & Gordon, 2003). In our case the first excited electronic state is far above the ground state, according to the TDDFT calculations, the first excitation energies are ~ 4.5 eV (Cs_3Br_3) and ~ 4.1 eV (Cs_3I_3). Therefore, the spin-orbit coupling was not taken into account in calculation of thermodynamic properties.

The calculated dissociation energies $\Delta_r E$, ZPVE corrections $\Delta_r \epsilon$, enthalpies of the dissociation reactions $\Delta_r H^\circ(0)$, and enthalpies of formation $\Delta_f H^\circ(0)$ of Cs_3X_3 molecules are presented in Table 4. The data determined previously for Cs_3F_3 (Mwanga et al., 2015a) and Cs_3Cl_3 (Mwanga et al., 2016) are included for comparison. Two types of dissociation reactions are considered: (i) into monomer and dimer and (ii) into three monomers. From fluoride to iodide the enthalpies of the dissociation reactions decrease: $129 \rightarrow 121 \rightarrow 117 \rightarrow 110$ kJ mol $^{-1}$ for the reactions (i), and $301 \rightarrow 276 \rightarrow 267 \rightarrow 253$ kJ mol $^{-1}$ for the reactions (ii). The second type of reactions requires approximately 2.3 times bigger energy than first one due to different number of bonds to be broken. The uncertainties of the $\Delta_r H^\circ(0)$ values may be estimated on the base of the comparison between theoretical and experimental data available for Cs_2Br_2 , Cs_2I_2 , $Cs_3I_2^+$, $Cs_2I_3^-$ (Mwanga et al., 2015b) and $Cs_4Cl_3^+$ (Mwanga et al., 2016) for which the maximum difference between the calculated MP4C method and experimental was equal to 16 kJ mol $^{-1}$. The enthalpies of formation $\Delta_f H^\circ(0)$ of the trimers found through both types of reactions are close to each other or coincide. The uncertainty is accepted to be ± 20 kJ mol $^{-1}$, and the values of $\Delta_f H^\circ(0)$ are as follows: -858 ± 20 kJ mol $^{-1}$ (Cs_3Br_3) and -698 ± 20 kJ mol $^{-1}$ (Cs_3I_3).

Table 4. The energies, $\Delta_r E$, ZPVE corrections, $\Delta_r \epsilon$, and enthalpies $\Delta_r H^\circ(0)$ of the dissociation reactions, and enthalpies of formation $\Delta_f H^\circ(0)$ of Cs_3X_3 (C_s) ($X = F, Cl, Br, I$) molecules, all values are in kJ mol $^{-1}$

No.	Dissociation reaction	$\Delta_r E$	$-\Delta_r \epsilon$	$\Delta_r H^\circ(0)$	$-\Delta_f H^\circ(0)$
1	$Cs_3F_3 = CsF + Cs_2F_2$	130.9	1.57	129	1,378
2	$Cs_3F_3 = 3CsF$	304.7	4.22	301	1,386
3	$Cs_3Cl_3 = CsCl + Cs_2Cl_2$	121.4	1.16	121	996
4	$Cs_3Cl_3 = 3CsCl$	278.3	2.76	276	996
5	$Cs_3Br_3 = CsBr + Cs_2Br_2$	117.5	0.98	117	858
6	$Cs_3Br_3 = 3CsBr$	268.7	2.14	267	858
7	$Cs_3I_3 = CsI + Cs_2I_2$	111.0	0.93	110	698
8	$Cs_3I_3 = 3CsI$	254.6	1.95	253	698

Notes: The values of $\Delta_r E$ and $\Delta_r \epsilon$ were obtained by MP4C and MP2 methods, respectively. The results for reactions 1–4 are based on our previous works (Mwanga et al., 2015a, 2016).

Table 5. Properties of neutral molecules Cs_4X_4 (distorted cubic, T_d), $X = Br, I$

Property	Cs_4Br_4		Cs_4I_4	
	B3LYP5	MP2	B3LYP5	MP2
$R_e(Cs-X)$	3.512	3.433	3.768	3.678
$\alpha_e(X-Cs-X)$	90.4	89.6	92.9	91.9
$\beta_e(Cs-X-Cs)$	89.6	90.4	87.1	88.0
$-E$	134.50200	133.96752	126.63848	126.04400
$\omega_1(A_1)$	89 (0)	83 (0)	53(0)	83 (0)
$\omega_2(A_1)$	46 (0)	31 (0)	36 (0)	36 (0)
$\omega_3(E)$	70 (0)	85 (0)	52 (0)	66 (0)
$\omega_4(E)$	35 (0)	35 (0)	24 (0)	37 (0)
$\omega_5(T_1)$	66 (0)	84 (0)	51 (0)	66 (0)
$\omega_6(T_2)$	89 (1.34)	95 (0.24)	66 (1.17)	82 (1.95)
$\omega_7(T_2)$	84 (2.66)	85 (3.75)	63 (1.59)	71 (0.71)
$\omega_8(T_2)$	36 (0.04)	19 (0.003)	26 (0.06)	26 (0.36)
$q(Cs)$	0.874	0.909	0.823	0.876
$q(X)$	-0.874	-0.909	-0.823	-0.876

3.2. Tetramers Cs_4Br_4 and Cs_4I_4 molecules

For the tetramers Cs_4X_4 molecules, only one equilibrium structure with T_d symmetry was confirmed to exist (Figure 1(c)). This structure is specified by two parameters $R_e(Cs-X)$ and $\alpha_e(X-Cs-X)$. The geometrical parameters and vibrational frequencies of Cs_4X_4 molecules are gathered in Table 5. Similar to trimers, the internuclear separation increases from bromide to iodide, while the corresponding vibrational frequencies decrease as a rule. Due to compactness of the tetramer structure, the deformational frequencies are not so low compared to trimers, both hexagonal and “butterfly-shaped”.

The IR spectra of Cs_4X_4 (T_d) are shown in Figure 5(a and b). One can see that only two modes are active: mode of high intensity at 85 cm^{-1} (Cs_4Br_4) and 82 cm^{-1} (Cs_4I_4) assigned to X-X wagging vibrations and the low intensive mode at 95 cm^{-1} (Cs_4Br_4) and 71 cm^{-1} (Cs_4I_4) which corresponds to Cs-X-Cs twisting vibrations.

The electron density distribution is represented through the Mulliken atomic charges q found by both methods, DFT and MP2 (Table 5). The values of q being about 0.8–0.9 au show a high ionic character of bonds. The observations discussed above for the trimer molecules are valid here as well; the magnitudes of q are higher by MP2 than DFT, the ionicity decreases from bromide to iodide. Compared to the trimer molecules, the charges in tetramers are slightly higher by 0.02–0.03 au.

Figure 5. Calculated IR spectra of distorted cube Cs_4X_4 (T_d): (a) Cs_4Br_4 and (b) Cs_4I_4 .

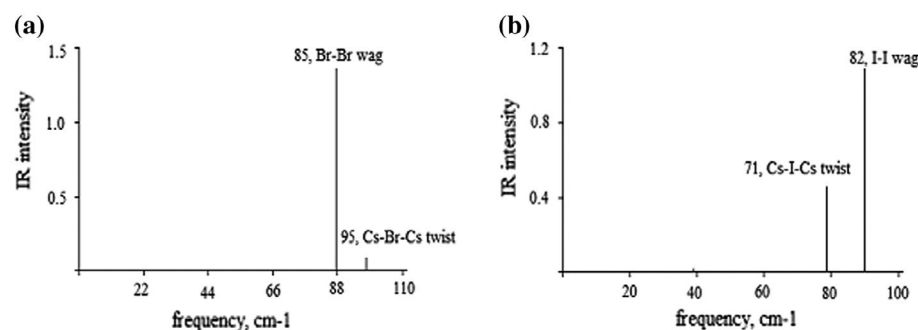


Table 6. The energies, $\Delta_r E$, ZPVE corrections, $\Delta_r \epsilon$, and enthalpies $\Delta_r H^\circ(0)$ of the dissociation reactions, and enthalpies of formation $\Delta_f H^\circ(0)$ of Cs_4X_4 (T_d) ($X = \text{F, Cl, Br, I}$) molecules, all values are in kJ mol^{-1}

No.	Dissociation reaction	$\Delta_r E$	$-\Delta_r \epsilon$	$\Delta_r H^\circ(0)$	$-\Delta_r H^\circ(0)$
1	$\text{Cs}_4\text{F}_4 = \text{CsF} + \text{Cs}_3\text{F}_3$	210.0	4.00	206	1,949
2	$\text{Cs}_4\text{F}_4 = 2\text{Cs}_2\text{F}_2$	169.8	2.66	167	1,941
3	$\text{Cs}_4\text{F}_4 = 4\text{CsF}$	517.4	7.96	509	1,956
4	$\text{Cs}_4\text{Cl}_4 = \text{CsCl} + \text{Cs}_3\text{Cl}_3$	219	2.15	217	1,453
5	$\text{Cs}_4\text{Cl}_4 = 2\text{Cs}_2\text{Cl}_2$	183.5	1.71	182	1,464
6	$\text{Cs}_4\text{Cl}_4 = 4\text{CsCl}$	497.3	4.9	492	1,453
7	$\text{Cs}_4\text{Br}_4 = \text{CsBr} + \text{Cs}_3\text{Br}_3$	213.0	3.43	210	1,265
8	$\text{Cs}_4\text{Br}_4 = 2\text{Cs}_2\text{Br}_2$	179.2	1.41	178	1,274
9	$\text{Cs}_4\text{Br}_4 = 4\text{CsBr}$	481.7	3.73	478	1,267
10	$\text{Cs}_4\text{I}_4 = \text{CsI} + \text{Cs}_3\text{I}_3$	192.6	1.81	191	1,038
11	$\text{Cs}_4\text{I}_4 = 2\text{Cs}_2\text{I}_2$	160.0	1.73	158	1,054
12	$\text{Cs}_4\text{I}_4 = 4\text{CsI}$	447.3	3.59	444	1,038

Notes: The values of $\Delta_r E$ and $\Delta_r \epsilon$ were obtained by MP4C and MP2 methods, respectively. The results for reactions 1–6 are based on our previous works (Mwanga et al., 2015a, 2016).

Three channels of the dissociation of Cs_4X_4 molecules with the elimination of monomer and dimer molecules were considered (Table 6), similarly to trimers, the data of our previous works were included (Mwanga et al., 2015a, 2016). It can be observed the dissociation into two Cs_2X_2 molecules requires lowest energy than other two channels. For the dissociation into two dimers, the values of $\Delta_r H^\circ(0)$ are less by 39 kJ mol^{-1} (Cs_4F_4), 35 kJ mol^{-1} (Cs_4Cl_4), 32 kJ mol^{-1} (Cs_4Br_4) and 33 kJ mol^{-1} (Cs_4I_4) compared to the dissociation into monomer plus trimer and by 342 kJ mol^{-1} (Cs_4F_4), 310 kJ mol^{-1} (Cs_4Cl_4), 300 kJ mol^{-1} (Cs_4Br_4) and 286 kJ mol^{-1} (Cs_4I_4) compared to the dissociation into four CsX molecules. Uncertainties of the enthalpies of reaction and enthalpies of formations were estimated as $\pm 20 \text{ kJ mol}^{-1}$ and $\pm 30 \text{ kJ mol}^{-1}$, respectively. The enthalpies of formation found on the base of three reactions are close to each other, the averaged values of $\Delta_f H^\circ(0)$ were accepted: $-1270 \pm 30 \text{ kJ mol}^{-1}$ (Cs_4Br_4) and $-1043 \pm 30 \text{ kJ mol}^{-1}$ (Cs_4I_4).

3.3. Trimer and tetramer dissociation: thermodynamic approach

For the most probable channels of dissociation of the clusters, the Gibbs free energies were calculated and plotted vs. temperature (Figures 6 and 7). The plots for other two halides, Cs_3X_3 and Cs_4X_4 ($X = \text{F}$ and Cl) were included. As seen, the values of $\Delta_r G^\circ$ are positive for rather narrow temperature range; the change of sign occurs at $\sim 330 \text{ K}$, 280 K , 240 K and 210 K for Cs_3X_3 and $\sim 390 \text{ K}$, 370 K , 360 K and 250 K for Cs_4X_4 ($X = \text{F, Cl, Br}$ and I), respectively. Therefore, according to the thermodynamic approach, only Cs_3F_3 and all tetramers excluding Cs_4I_4 may exist at the room and moderate temperatures. With temperature rise, all trimers Cs_3X_3 dissociate spontaneously into CsX plus Cs_2X_2 while tetramers Cs_4X_4 decompose into two dimeric molecules.

Figure 6. Gibbs free energy change vs. temperature for the reaction $\text{Cs}_3\text{X}_3 = \text{CsX} + \text{Cs}_2\text{X}_2$ ($X = \text{F, Cl, Br}$ and I).

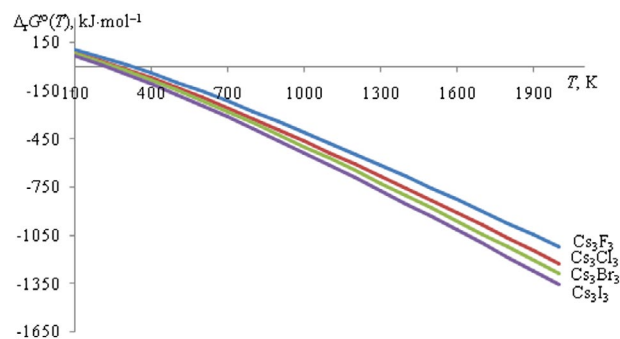
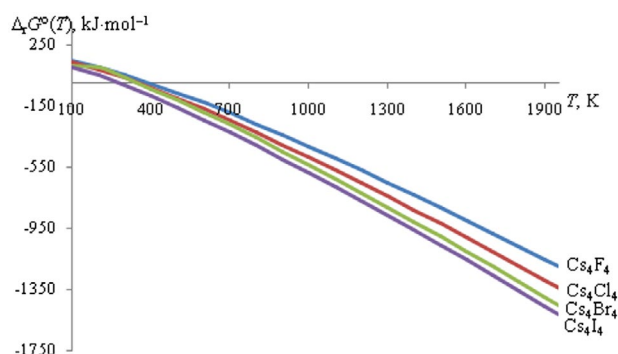


Figure 7. Gibbs free energy change vs. temperature for the reaction $Cs_4X_4 = 2Cs_2X_2$ (X = F, Cl, Br and I).



4. Conclusion

The geometrical structure and vibrational spectra of the trimer and tetramer molecules, Cs_3X_3 and Cs_4X_4 (X = Br and I), were determined by DFT/B3LYP5 and MP2 methods; the results were in a good accordance, as a rule, between each other and also with experimental and theoretical data available in literature. Regarding the enthalpies of dissociation reactions, the MP2 method was more preferable compared to DFT; the BSSE correction was to be taken into account. The existence of two isomeric forms, hexagonal and “butterfly-shaped”, for Cs_3X_3 was confirmed, and the latter isomer was found to prevail in equilibrium vapour. Thermodynamic properties of Cs_3X_3 and Cs_4X_4 were calculated. Different dissociation channels were considered; among them the routes with elimination of dimeric molecules appeared to be most feasible. The analysis of Gibbs free energy $\Delta_r G^\circ$ revealed that these clusters are not stable at elevated temperatures; at temperatures greater than ~400 K both Cs_3X_3 and Cs_4X_4 dissociate spontaneously into CsX plus Cs_2X_2 and two dimer molecules, respectively. Tetramers are more stable than trimers, likely due to compact cubic structure.

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