Theoretical Study of Cluster Ions Existing in Vapours over Cesium Bromide and Iodide

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Authors’ contributions

This work was carried out in collaboration between all authors. Author SFM performed computations, wrote the first draft of the manuscript and managed literature searches. Author TPP performed corrections and some selected computations regarding the structure and vibrational spectra. Author AMP performed some selected thermodynamic calculations. All authors analyzed and discussed the results and approved the final manuscript.

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ABSTRACT

The properties of ions Cs₂X⁺, Cs₃X₂⁺, CsX₂⁻, and Cs₂X₃⁻ (X = Br or I) have been studied using the density functional theory and Möller–Plesset perturbation theory of the 2nd and 4th order. For all species the equilibrium geometrical configurations and vibration frequencies were determined. Different isomers of pentaatomic ions were found to exist: the linear (D∞h), V-shaped (C₂v), kite-shaped (C₂v) and bipyramidal (D₃h). The relative abundances of isomers were calculated for temperatures between 700 K and 1600 K. It was found that at about 800 K, the amount of different isomers was comparable for Cs₃Br₂⁺, Cs₃I₂⁺ and Cs₂I₃⁻ ions, while for Cs₂Br₃⁻ the linear isomer was proved to be predominant. The enthalpies of dissociation reactions with elimination of CsX molecules and the enthalpies of formation of ions were determined.

Keywords: Cluster ions; cesium bromide; cesium iodide; isomers; enthalpies of formation of ions; enthalpies of dissociation reactions.
1. INTRODUCTION

Alkali halide cluster ions form a potential group for researches due to the possibilities of designing and fabricating new materials. Some of these cluster ions have unique properties such as electronic, optical and magnetic which are function of size and composition [1-3]. These species can serve as fundamental building blocks for a new class of materials with desired properties [3,4].

Different species composed of cesium and iodine are proved to exist among the fission products that can be released in nuclear power plants [5-8]. They have major impact on ground contamination and radiation doses in the environment in case of accidents such as containment building leakages. They are highly radioactive in short term for iodine and in middle term for cesium [5,6,9]. Thus, evaluations of their thermodynamic properties are essential for safety features of the nuclear pressurized water reactor.

Considerable studies of alkali halide cluster ions have been done in the past decades [4,10-15]. Different analytical procedures have been employed for the investigation of ionic clusters [16,17]. Mass spectrometry stands as a major experimental technique which is capable of analyzing a broad characterization of their properties [18]. Various positive and negative ions had been identified in equilibrium vapours using high temperature mass spectrometry [19-25]. For the treatment of experimental data thermodynamic functions of molecules and ions are required and for the calculation of the thermodynamic functions the geometrical parameters and vibrational frequencies are needed. However they are difficult to be measured by available experimental techniques [26].

Quantum chemical methods are proficient to provide accurate information required. Previously the structure and properties of cluster ions existing in saturated vapors over sodium fluoride (NaF), sodium chloride (NaCl), sodium bromide (NaBr), sodium iodide (NaI), potassium chloride (KCl), rubidium chloride (RbCl) and cesium chloride (CsCl) had been studied by Pogrebnaya et al. [27-30] using quantum chemical methods.

The ionic species Cs\(^{+}\), Cs\(^{+}\), Cs\(_{2}\)I\(^{-}\), I\(^{-}\), CsI\(_{2}\)\(^{-}\), and Cs\(_{2}\)I\(^{-}\) have been detected in the saturated vapour over cesium iodide by high temperature mass spectrometry [24,31]. Photoelectron spectroscopy was applied to CsI\(_{2}\) [32]. The ions Cs\(_{3}\)I\(^{+}\) and CsI\(_{2}\)\(^{-}\) were resulted from collisions of Cs\(_{2}\)I\(_{2}\) with Xe [33]. In line to this, we expect similar ions to exist in saturated vapour over cesium bromide. Thus the aims of the present work were to determine the characteristics of the cluster ions of cesium bromide and iodide using quantum chemical methods, as well as to calculate the thermodynamic properties of the ions. To verify the reliability of the results obtained, the properties of neutral species CsX and Cs\(_{2}\)X\(_{2}\) have been calculated and analyzed through a comparison with the available reference data.

2. COMPUTATIONAL DETAILS

The calculations were performed by GAMESS (General Atomic and Molecular Electronic Structure System) program [34], Firefly version 8.0.0 [35], employing electron density functional theory (DFT) with the Becke–Lee–Yang–Parr functional (B3LYP5) [36,37] and Becke-Perdew functional (B3P86) [37-39], as well as the second order and fourth order Möller–Plesset perturbation theory (MP2 and MP4). The effective core potential (Cs ECP GEN 46 3, 9 electrons in the core) with Def2-QZVP basis set (6s5p4d1f) [40] for Cs and the relativistic effective core potentials (Br ECP GEN 28 4, 7 electrons in the core; I ECP GEN 46 4, 7 electrons in the core) with SDB-aug-cc-pVTZ basis set (4s4p3d2f) [41] taken from EMSL (The Environmental Molecular Sciences Laboratory, U.S.) [42-44] were used. The B3LYP5 and MP2 methods were applied to compute the geometrical parameters and vibrational spectra of cluster ions. The geometrical structures determined are confirmed as corresponding to minima energy by the absence of imaginary frequencies.

The dissociation energies \( \Delta E \) were calculated by B3LYP5, B3P86 and MP2 methods. Also more advanced MP4 level was employed, the equilibrium geometrical structure found by MP2 method was used. Furthermore, the correction for basis set superposition error (BSSE) [45] has been taken into account for MP2 and MP4 methods using the procedure proposed in [46]. The methods of calculations with BSSE corrections are denoted hereafter as MP2C and MP4C.
3. RESULTS AND DISCUSSION

3.1 Molecular Properties of CsX and Cs₂X₂ (X = Br or I)

For the monomer molecules CsBr and CsI, the properties such as geometrical parameters, normal vibrational frequencies, dipole moments and ionization energies have been computed using the B3LYP5 and MP2 methods. The results are compared with available reference data (Table 1) which include the experimental [47,48] and found by a high level quantum chemical calculation [6] as well. For both CsBr and CsI molecules, the internuclear distances $R_e$ (Cs–X) calculated by us are longer than the reference values. The B3P86 method gives better results when comparing with the values obtained from microwave spectrum however overestimating it by 0.02 Å for both CsBr and CsI. While the MP2 method is also close to the experimental value of microwave spectrum since it was longer by 0.03 Å for CsBr and 0.04 Å for CsI. The difference in the reference data themselves are about 0.02 Å for CsBr and 0.01 Å for CsI. The calculated values of the normal vibrational frequencies $\omega_a$ are related to the internuclear separations: the bigger is the distance, the smaller the frequency. The values of frequencies computed by all three methods B3LYP5, MP2 and B3P86 are in agreement with the reference values, the MP2 being preferred.

The ionization energies were calculated as energy differences between the parent and ionized species. The results obtained by three theoretical levels are in agreement between each other and with the experimental values [47-50] as well. As for the dipole moment, the theoretical results do not contradict to the experimental data, the B3LYP5 level being in better agreement.

For the dimer molecules Cs₂Br₂ and Cs₂I₂ the structure was proved to be planar cycle (rhomb) with symmetry $D_{2h}$ (Fig. 1a) that is in accordance with Hargittai [51] and Dickey et al. [52] reported that all dimers geometries of alkali halides have $D_{2h}$ symmetry. The calculated and reference data for Cs₂X₂ molecules are gathered in Table 2: geometrical parameters, vibrational frequencies, IR intensities and enthalpies of dissociation.

The internuclear distances $R_e$ (Cs–X) found by MP2 and both DFT methods are in agreement with the literature values taking into account the scatter of about 0.06 Å of the reference data themselves. It is worth to mention that following the general trend in our data which are usually overrated compared with reference values, the theoretical results by Badawi et al. [6], $R_e$(Cs–Br) = 3.296 Å and $R_e$(Cs–I) = 3.511 Å, seem to be more realistic and preferable for both dimers while the experimental values of $R_e$(Cs–Br) = 3.356 Å found by electron diffraction study [48] and $R_e$(Cs–I) = 3.572 Å [53] both look overrated.

The experimental vibrational frequencies are confined by two values of $\omega_1$ ($A_g$) and $\omega_3$ ($B_{3u}$) for Cs₂Br₂ [50] and four values $\omega_1$ ($A_g$), $\omega_4$ ($B_{1u}$), $\omega_5$ ($B_{3u}$), and $\omega_3$ ($B_{3u}$) for Cs₂I₂ [50,53,54]. The theoretical values of $\omega_1$ [6] are taken into account as well. We can notice that theoretical frequencies computed by us are in a good agreement with the reference values.

Concluding this section about the geometrical parameters and frequencies of the dimer molecules, we can state that all three methods, B3LYP5, B3P86 and MP2, give reasonable results in most cases, nevertheless MP2 method provides less deviation from the reference data.

| Property                | CsBr | Reference | B3LYP5 | B3P86 | MP2 | Reference |
|-------------------------|------|-----------|--------|-------|-----|-----------|
| $R_e$(Cs–X), Å           | 3.124| 3.094     | 3.105  | 3.072 | 48, 49|           |
|                         |      |           |        |       |     |           |
|                         |      |           |        | 3.072 | [48, 49]|          |
|                         |      |           |        | 3.099 | [48]  |          |
|                         |      |           |        | 3.087 | [48]  |          |
|                         |      |           |        | 3.372 |       | 3.315     |
|                         |      |           |        |       |       | [47, 49]|          |
|                         |      |           |        | 3.314 | [47]  |          |
|                         |      |           |        | 3.303 | [6]   |          |
| $\omega_a$, cm$^{-1}$    | 141  | 144       | 145    | 150   | [49] |           |
|                         |      |           |        | 144   | [6]   |          |
|                         |      |           |        | 141   | [50]  |          |
|                         |      |           |        | 111   |       | 119       |
|                         |      |           |        |       |       | [47, 49]|          |
|                         |      |           |        | 118   | [6]   |          |
|                         |      |           |        | 117   | [50]  |          |
| $\mu_e$, D              | 10.9 | 10.7      | 11.3   | 10.8  | [48, 49]|           |
|                         |      |           |        | 11.6  |       | 11.6      |
|                         |      |           |        |       |       | [49]      |
| $IP$, eV                | 7.99 | 8.21      | 8.03   | 8.12  | [48, 49]|           |
|                         |      |           |        | 7.45  |       | 7.54      |
|                         |      |           |        | 7.68  |       |           |
|                         |      |           |        | 7.46  |       |           |

Notes: $R_e$(Cs–X) is the equilibrium internuclear distance; $\omega_a$ is the normal mode frequency, $\mu_e$ is the dipole moment, $IP$ is the ionization potential.

*Microwave spectrum; *Electron diffraction method; *high level quantum chemical computation; *IR matrix isolation studies (Kr, Xe)
Therefore we expect the similar trend to appear in the properties of the ions considered further when the same level of computational method is applied.

The energies of dissociation reactions $\Delta E$ of Cs$_2$X$_2$ into CsX molecules have been calculated using different theoretical levels: B3LYP5, B3P86, MP2, MP2C, MP4, and MP4C. The enthalpies of reactions $\Delta H^\circ(0)$ were obtained using the energies $\Delta E$, and the zero-point vibration energy (ZPVE) correction $\Delta \varepsilon$ as given in following equations

$$\Delta H^\circ(0) = \Delta E + \Delta \varepsilon,$$

$$\Delta \varepsilon = \frac{1}{2} \hbar c (\Sigma \omega_{i\text{ prod}} - \Sigma \omega_{i\text{ react}}),$$

where $\hbar$ is the Plank’s constant, $c$ is the speed of light in the free space, $\Sigma \omega_{i\text{ prod}}$ and $\Sigma \omega_{i\text{ react}}$ are the sums of the vibration frequencies of the products and reactants, respectively.

The theoretical enthalpies of dissociations are compared with the reference values $\Delta H^\circ(0) = 153.5$ kJ mol$^{-1}$ (Cs$_2$Br$_2$) and 150.9 kJ mol$^{-1}$ (Cs$_2$I$_2$), accessed from the IVTANTHERMO Database [55]. Beside we take into consideration here the results of a high level quantum chemical computation [6]: 154.7 kJ mol$^{-1}$ (Cs$_2$Br$_2$) and 147.1 kJ mol$^{-1}$ (Cs$_2$I$_2$). The comparison is presented in Figs. 2a and 2b where the experimental values from [55] are taken as a benchmark and the differences $\Delta$ between the theoretical and reference values are depicted by the bar diagrams. As one can see, B3LYP5 and B3P86 methods give underrated results for both dimeric species while MP2C and MP4 demonstrate rather good agreement. According to our highest level of computation, MP4C, $\Delta = -3.5$ kJ mol$^{-1}$ and $\sim 8.4$ kJ mol$^{-1}$ for Cs$_2$Br$_2$ and Cs$_2$I$_2$ respectively. Based on these results, and assuming a factor of 1.5, we estimated uncertainties to be $\pm 5$ kJ mol$^{-1}$ and $\pm 13$ kJ mol$^{-1}$ to the corresponding theoretical values of $\Delta H^\circ(0)$ calculated by MP4C. It should be noted also that our result found by MP4C method for Cs$_2$Br$_2$ is in a good agreement with both reference data [55] and [6]. For Cs$_2$I$_2$ the agreement between the value 153$\pm$13 and experimental one, 150.9 [55], is worse, but within the uncertainties, there is no contradiction. If we take into account the data from [6] as a benchmark the agreement appeared to be better as seen in Fig. 2 c. Moreover the bar diagram in Fig. 2 c for cesium
iodide now looks alike to that of bromide (Fig. 2 a).

It is also worth to note here that the difference between the enthalpies of dissociation reactions $\Delta H^\circ(0)$ for Cs$_2$Br$_2$ and Cs$_2$I$_2$ is 7 kJ mol$^{-1}$ according to our results which agrees well with ~8 kJ mol$^{-1}$ as reported recently by Roki et al. [6]. The last value seems to be more feasible than 2.6 kJ mol$^{-1}$ as it comes from [55]. The result of $\Delta H^\circ(0) = 164.1$ kJ mol$^{-1}$ found for Cs$_2$I$_2$ on the base of the data $\Delta H^\circ$(CsI, g, 298.15 K) = –153.3±1.8 and $\Delta H^\circ$(CsBr$_2$, g, 298.15 K) = –469.2±5 kJ mol$^{-1}$ seems to be more feasible than 2.6 kJ mol$^{-1}$ as it comes from [55]. The last value seems to be more feasible than 2.6 kJ mol$^{-1}$ as it comes from [55]. The result of $\Delta H^\circ(0) = 164.1$ kJ mol$^{-1}$ found for Cs$_2$I$_2$ on the base of the data $\Delta H^\circ$(CsI, g, 298.15 K) = –153.3±1.8 and $\Delta H^\circ$(CsBr$_2$, g, 298.15 K) = –469.2±5 kJ mol$^{-1}$ reported recently by Roki et al. [7] is evidently higher than the enthalpy of dissociation of cesium bromide and therefore looks like overrated.

### 3.2 Geometrical Structure and Vibrational Spectra of the Cluster Ions

For the calculation of the properties of the cluster ions two methods; DFT (B3LYP5) and MP2 have been used. As a whole array of the data obtained for the neutral species, triatomic and pentaatomic, positive and negative ions demonstrates alike trends from DFT to MP2 levels, therefore we present hereafter the results found by more reliable MP2 method.

#### 3.2.1 Triatomic ions Cs$_2$X$^+$ and CsX$^-$

Linear structures with $D_{\text{ib}}$ symmetry are proved to exist for the triatomic ions (Fig. 1 b, c). The properties such as equilibrium internuclear separations $R_\text{e}(\text{Cs}–\text{X})$, the frequencies of normal vibrations $\omega_i$, and the intensities of vibrations in IR spectra $I_i$ have been determined and given in Table 3.

It can be observed that internuclear separation $R_\text{e}(\text{Cs}–\text{X})$ increases by ~0.08 Å from positive to negative ions for both species. Also an increase of internuclear distances by ~0.25 Å has been featured across both positive and negative cesium bromide to cesium iodide. Clearly the increase of internuclear distance from positive to negative ions is due to an excess negative charge in the CsX$^-$ ion, and from cesium bromide to cesium iodide is due to an extra shell. This increase in the internuclear distance corresponds to the decrease in the antisymmetric stretching frequency $\omega_2$: 138 cm$^{-1}$ (Cs$_2$Br$^+$) to 109 cm$^{-1}$ (CsI$^+$); and 113 cm$^{-1}$ (CsBr$_2$) to 98 cm$^{-1}$ (CsI$_2$).

#### Table 3. Properties of the triatomic ions with linear configuration ($D_{\text{ib}}$), MP2 results

| Property | Cs$_2$Br$^+$ | CsBr$_2$ | CsI$^+$ | CsI$_2$ |
|----------|---------------|-----------|----------|----------|
| $R_\text{e}(\text{Cs}–\text{X})$ | 3.264 | 3.345 | 3.509 | 3.590 |
| $\omega_1$ ($\Sigma_u^+$) | 70 | 88 | 65 | 65 |
| $\omega_2$ ($\Sigma_u^+$) | 138 | 113 | 109 | 98 |
| $\omega_3$ ($\Pi_u$) | 24 | 14 | 19 | 14 |
| $I_2$ | 1.11 | 1.13 | 0.81 | 0.78 |
| $I_3$ | 0.31 | 0.41 | 0.25 | 0.27 |

Notes: $R_\text{e}(\text{Cs}–\text{X})$ is the internuclear separation, $\lambda$; $\omega_i$ are the fundamental frequencies, cm$^{-1}$; $I_i$ are the IR intensities, $D^2$ amu$^{-1}$ Å$^{-2}$.
3.2.2 Pentaatomic ions, Cs$_3X_2^+$ and Cs$_3X_2^-$

Three different possible configurations have been considered (Fig. 3): linear of $D_{\infty h}$ symmetry (I), planar cyclic (kite-shaped), $C_{2v}$ (II), and bipyramidal, $D_{3h}$ (III). For each structure, the geometrical parameters were optimized and fundamental frequencies were determined.

As concerns the linear configuration for the Cs$_3$Br$_2^+$ ion the imaginary frequencies have been revealed. The further optimization showed the bent (V-shaped) structure of $C_{2v}$ symmetry to exist with the valence angle $\alpha$ (Br–Cs–Br) = 144° and practically without decrease in energy compared to the linear shape within the accuracy of optimization procedure. Other pentaatomic ions, Cs$_3$Br$_3^+$, Cs$_3$I$_2^+$, and Cs$_3$I$_3^-$, were confirmed to be linear. Note these two equilibrium structures were obtained disregarding initial configuration started from: linear, bent or five-membered ring structures were converted during the optimization into V-shaped for Cs$_3$Br$_2^+$ or linear for other three ions. Here and hereafter we
Call the isomer I as the ion of the bent (V-shaped) structure \((C_2v)\) for the \(Cs_2Br_2^+\) ion and linear \((D_{\infty h})\) for \(CsBr_3^+\), \(CsI_2^+\), and \(CsI_3^–\); their properties are given in Table 4. There are two different internuclear separations, terminal and bridge, which are denoted as \(R_{\text{e}}(Cs−X)\) and \(R_{\text{br}}(Cs−X)\), respectively. From positive to negative ions of cesium iodide, there is a slight increase in the internuclear distance by 0.07 Å and 0.05 Å for \(CsBr\) and \(CsBr\), respectively. The similar increase is observed for cesium iodide. Regarding terminal and bridge distances, for both ions the first one is shorter than the second, by ~0.16 Å for \(Cs_2X^+\) and by ~0.13 Å for \(Cs_2X^−\). In vibrational spectra of the ions with linear or V-shaped structure, several low deformational frequencies are observed, that gives evidence that these structures are floppy regarding to bending of the central moiety.

The isomer II, planar cyclic \((C_3v)\), and isomer III, bipyramidal \((D_{3h})\), were also found to correspond to minima at the potential energy surface (PES). The optimized geometrical parameters were located and all calculated vibrational frequencies were confirmed to be real. Tables 5 and 6 report the properties of the ions \(Cs_2X^+\) and \(Cs_2X^−\) for cyclic and bipyramidal structures, their geometrical configurations are shown in Figs. 3 c, d, e, and f.

The cyclic structure is described by three different internuclear separations \(Cs−X\), which are denoted as \(R_{\text{t}}\), \(R_{\text{c}}\), and \(R_{\text{br}}\), and two independent valence angles \(\alpha_\theta\) and \(\beta_\theta\). The internuclear distances of the negative ions are slightly greater than those of positive ions correspondingly. The relative energy of the cyclic isomers with respect to the isomer I is \(\Delta E_{\text{iso}} = E_{\text{iso}} - E_{\text{i}}\) and for all four ions the values of \(\Delta E_{\text{iso}}\) are negative and lie in the range between ~8 and ~12 kJ·mol\(^{-1}\). This result indicates that the cyclic isomer has lower energy on the PES than the isomer I and is more stable energetically. The vibrational spectra look alike for positive and negative ions both in frequencies and IR intensities.

The isomer III, that is of the bipyramidal shape, is specified by two parameters that are internuclear distance \(R_{\text{e}}(Cs−X)\) and valence angle \(\alpha_\theta\). The internuclear distances for positive ions are slightly shorter than those for negative ions for cesium bromide or equal for iodide. We refer to the magnitudes of ionic radii of \(Cs^+, Br^+, I^−\) ions. The bond angles at the vertices are almost the same and close to right angle. The corresponding vibrational frequencies of \(Cs_2X^+\) and \(Cs_2X^−\) ions are close to each other while the frequencies of positive ions are slightly larger than those of negative. The relative energy of bipyramidal isomer with respect to the isomer I is \(\triangle E_{\text{iso}} = E_{\text{iso}} - E_{\text{i}}\), the values of \(\Delta E_{\text{iso}}\) are negative and in the range between ~30 and ~38 kJ·mol\(^{-1}\). Therefore the isomer III is more energetically stable than the linear one for \(CsBr_3^+, CsI_2^+, Cs_2I_3^−\), and \(V\)-shaped for \(Cs_2Br_2^+\). In addition the bipyramidal isomer has lower energy than cyclic one and thus appeared to be the most energetically stable among three alternative isomers.

| Property | \(Cs_2Br_2^+(C_{2v})\) | Property | \(Cs_2Br_2^−(D_{\infty h})\) | \(CsI_2^+(D_{3h})\) | \(CsI_3^−(D_{3h})\) |
|----------|-------------------------|----------|------------------------|-------------------|-------------------|
| \(R_{\text{e}}(Cs−X)\) | 3.216 | \(R_{\text{e}}(Cs−X)\) | 3.282 | 3.467 | 3.530 |
| \(R_{\text{br}}(Cs−X)\) | 3.371 | \(R_{\text{br}}(Cs−X)\) | 3.416 | 3.622 | 3.652 |
| \(\alpha_{\theta}(Br−Cs−Br)\) | 143.6 | | | | |
| \(\beta_{\theta}(Cs−Br−Cs)\) | 179.5 | | | | |
| \(\omega_1(A_1)\) | 138 | \(\omega_1(S'\beta)\) | 117 | 106 | 98 |
| \(\omega_2(A_1)\) | 51 | \(\omega_2(S'\beta)\) | 45 | 34 | 33 |
| \(\omega_3(A_1)\) | 25 | \(\omega_3(S'\beta)\) | 121 | 110 | 101 |
| \(\omega_4(A_1)\) | 8 | \(\omega_4(S'\beta)\) | 103 | 74 | 76 |
| \(\omega_5(A_2)\) | 23 | \(\omega_5(\Pi g)\) | 10 | 13 | 14 |
| \(\omega_6(B_2)\) | 24 | \(\omega_6(\Pi u)\) | 20 | 20 | 16 |
| \(\omega_7(B_2)\) | 137 | \(\omega_7(\Pi u)\) | 3 | 8 | 10 |
| \(\omega_8(B_2)\) | 79 | | | | |
| \(\omega_9(B_2)\) | 23 | | | | |
| \(\mu_\sigma\) | 9.9 | | | | |

Notes: \(R_{\text{e}}(Cs−X)\) and \(R_{\text{br}}(Cs−X)\) are the terminal and bridge internuclear distances respectively, \(\alpha_{\theta}(Br−Cs−Br)\) and \(\beta_{\theta}(Cs−Br−Cs)\) are the valence angles in degrees; \(\omega\) are the fundamental frequencies, cm\(^{-1}\); \(\mu_\sigma\) is the dipole moment, D.
3.3 Relative Concentration of Isomers

To examine the relative concentrations of isomers I, II, and III in saturated vapours over cesium bromide or iodide, thermodynamic calculations were performed. We considered the isomerization reactions I → II and I → III. The relative concentrations \( x_i \) of the two isomers in equilibrium vapour was calculated using the following formula:

\[
\Delta H^\circ(0) = T \Delta \Phi^\circ(T) - R T \ln x_i
\]  

where \( \Delta H^\circ(0) \) is the enthalpy of the reaction; \( T \) is absolute temperature; \( \Delta \Phi^\circ(T) \) is the change in the reduced Gibbs energy of the reaction, \( \Phi^\circ(T) = -[H^\circ(T) - H^\circ(0) - TS^\circ(T)]/T; \ x_i = p_i/p; \ p_i \) is the partial pressure of the isomer II or III, and \( p_i \) is the partial pressure of the isomer I. Hence here we have two ratios to be considered for each of the pentaatomic ions: \( x_{II} = p_{II}/p \) and \( x_{III} = p_{III}/p \).

The enthalpies of the isomerization reactions \( \Delta H^\circ(0) \) were evaluated using isomerization energies \( \Delta E_{iso} \) and the ZPVE corrections \( \Delta \epsilon \) by use of Eqs. (1) and (2); the energies \( \Delta E_{iso} \) were calculated by MP4 method. The values of \( \Delta \Phi^\circ(T) \) and other thermodynamic functions were calculated in the rigid rotator-harmonic oscillator approximation using the optimized coordinates and vibrational frequencies obtained in the MP2 calculations as the input parameters. The values of reduced Gibbs free energy and other thermodynamic functions are reported in the APPENDIX. The thermodynamic functions and

### Table 5. Properties of the pentaatomic ions with cyclic structure of C\(_{3\nu}\) symmetry (isomer II), MP2 results

| Property          | Cs\(_3\)Br\(_2\)\(^+\) | Cs\(_3\)Br\(_3\)\(^-\) | Cs\(_3\)J\(_2\)\(^+\) | Cs\(_3\)J\(_3\)\(^-\) |
|-------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| \( R_{\alpha}(\text{Cs-X}) \) | 3.255                   | 3.270                   | 3.510                   | 3.521                   |
| \( R_{\beta}(\text{Cs-X}) \) | 3.295                   | 3.336                   | 3.548                   | 3.585                   |
| \( R_{\gamma}(\text{Cs-X}) \) | 3.557                   | 3.603                   | 3.797                   | 3.846                   |
| \( \alpha_e \)    | 85.6                    | 86.8                    | 88.1                    | 84.6                    |
| \( \beta_e \)     | 99.9                    | 99.1                    | 96.5                    | 100.9                   |
| \( \gamma_e \)    | 135.5                   | 136.3                   | 136.4                   | 135.1                   |
| \( \Delta E_{iso} \) | -8.4                   | -11.6                   | -9.2                    | -10.9                   |
| \( \omega_1(A_1^\prime) \) | 116                    | 114                     | 92                      | 91                      |
| \( \omega_2(A_1^\prime) \) | 111                    | 105                     | 90                      | 88                      |
| \( \omega_3(A_1^\prime) \) | 56                     | 65                      | 51                      | 50                      |
| \( \omega_4(A_1^\prime) \) | 31                     | 31                      | 25                      | 26                      |
| \( \omega_5(B_1) \) | 33                     | 29                      | 24                      | 25                      |
| \( \omega_6(B_1) \) | 14                     | 10                      | 11                      | 8                       |
| \( \omega_7(B_2) \) | 118                    | 112                     | 95                      | 93                      |
| \( \omega_8(B_2) \) | 65                     | 64                      | 55                      | 54                      |
| \( \omega_9(B_2) \) | 18                     | 22                      | 16                      | 17                      |
| \( \mu_e \)       | 9.4                    | 6.7                     | 10.8                    | 7.8                     |

Notes: \( R_{\alpha}(\text{Cs-X}) \), \( R_{\beta}(\text{Cs-X}) \), and \( R_{\gamma}(\text{Cs-X}) \) are internuclear distances, \( \alpha_e \), \( \beta_e \), and \( \gamma_e \) are the valence angles in degrees; \( \Delta E_{iso} = E_{II} - E_I \) is the relative energy of the cyclic isomer, kJ mol\(^{-1}\); \( \omega_i \) are the normal mode frequencies, cm\(^{-1}\); \( \mu_e \) is the dipole moment, D.

### Table 6. Properties of the pentaatomic ions with bipyramidal structure of D\(_{3h}\) symmetry (isomer III), MP2 results

| Property          | Cs\(_3\)Br\(_2\)\(^+\) | Cs\(_3\)Br\(_3\)\(^-\) | Cs\(_3\)J\(_2\)\(^+\) | Cs\(_3\)J\(_3\)\(^-\) |
|-------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| \( R_{\alpha}(\text{Cs-X}) \) | 3.373                   | 3.415                   | 3.673                   | 3.668                   |
| \( \alpha_e \)    | 90.0                    | 89.7                    | 88.2                    | 92.5                    |
| \( \Delta E_{iso} \) | -30.32                 | -38.48                  | -35.54                  | -38.14                  |
| \( \omega_1(A_1^\prime) \) | 111                    | 104                     | 86                      | 84                      |
| \( \omega_2(A_1^\prime) \) | 52                     | 54                      | 49                      | 43                      |
| \( \omega_3(A_2^\prime) \) | 101                    | 98                      | 73                      | 71                      |
| \( \omega_4(E^\prime) \) | 99                     | 97                      | 75                      | 80                      |
| \( \omega_5(E^\prime) \) | 29                     | 39                      | 29                      | 25                      |
| \( \omega_6(E^\prime) \) | 77                     | 67                      | 57                      | 58                      |

Notes: \( R_{\alpha}(\text{Cs-X}) \) is the internuclear distance, \( \alpha_e \) is the valence angle in degrees; \( \Delta E_{iso} = E_{III} - E_I \) is the relative energy of the bipyramidal isomer, kJ mol\(^{-1}\); \( \omega_i \) are the normal mode frequencies, cm\(^{-1}\)
the relative concentration of the isomers were computed for the temperature range between 700 K and 1600 K related to the experimental condition. The results of calculations of energies and enthalpies of the isomerization reactions $\Delta_r H^\circ(0)$, ZPVE corrections $\Delta \varepsilon$, change in the reduced Gibbs free energies $\Delta_r \Phi^\circ(T)$, and relative concentration $x_i = p_i/p_i$ the isomers are reported in Table 7 for $T = 800$ K.

For each isomerization reaction considered the value of $\Delta_r H^\circ(0)$ is negative which means that the isomer in the right hand side of the reactions is more favorable by energy regarding the isomer I. Compared to the results found by the MP2 method the magnitudes of $\Delta_r H^\circ(0)$ by MP4 level are less and are in the range $\sim 20-30$ kJ mol$^{-1}$ for the bipyramidal isomer and $\sim 5-8$ kJ mol$^{-1}$ for cyclic isomer.

![Diagram of isomers](image_url)

**Fig. 3.** Geometrical equilibrium structures of the isomers for pentaatomic ions: (a) V-shaped, C$_{2v}$, Cs$_3$Br$_2^+$, (b) linear, D$_{sh}$, Cs$_2$Br$_3^-$, Cs$_3$I$_2^+$, and Cs$_2$I$_3^-$, (c) planar cyclic, C$_{2v}$, Cs$_3$X$_2^+$, (d) planar cyclic, C$_{2v}$, Cs$_2$X$_3^-$, (e) bipyramidal, D$_{3h}$, Cs$_3$X$_2^+$, (f) bipyramidal, D$_{3h}$, Cs$_2$X$_3^-$
The value of \( x_i \) represents which isomer out of two is prevailing in the saturated vapour. One can see that \( x_i < 1 \) for all of the isomerization reactions that implies the isomer I is prevailing compared to the cyclic or bipyramidal. It is important to note here that for the ions \( \text{Cs}_3\text{Br}_2^- \), \( \text{Cs}_3\text{I}_2^- \), and \( \text{Cs}_3\text{I}_3^- \) the isomers I and II are found in comparable amount, but the bipyramidal one is not abundant. For the ion \( \text{Cs}_3\text{Br}_3^- \) the linear isomer is the most abundant compared with two others and actually only this one among the three exists.

The temperature dependence of the relative concentration \( x_i \) has been examined for the temperature range between 700 and 1600 K (Fig. 4). As is seen all relative concentrations of the isomers decrease with temperature increase. For the ion \( \text{Cs}_3\text{Br}_2^- \) at 800 K, the concentration of cyclic isomer is 27% and decreases slowly to about 18% at 1500 K (Fig. 4 a). The concentrations of bipyramidal \( \text{Cs}_3\text{Br}_2^- \) is 3% at 800 K and decreases to 0.7% at 1500 K. For the negative ion \( \text{Cs}_3\text{Br}_3^- \) the concentrations of both cyclic and bipyramidal are very low and decrease further with temperature rise (Fig. 4 b). For the ions \( \text{Cs}_3\text{I}_2^- \) and \( \text{Cs}_3\text{I}_3^- \), a very close appearance of the plots is observed in Figs 4 c, d. There is rather big amount of both cyclic and bipyramidal isomers at temperatures around 700-800 K, and then the relative concentrations are dropping down rapidly when the temperature rises still remaining essential for the cyclic species.

As the three isomers may occur in a comparable amount, the fraction \( w_i \) of each isomer out of three was found as well using the following equation:

\[
 w_i = \frac{p_i}{p_1 + p_{II} + p_{III}},
\]

where \( p_i \) (i = I, II, or III) represents the concentration of the isomer of interest. The fraction \( w_i \) was expressed through the ratio \( x_i = p_i / p_i \) mentioned above:

\[
 w_i = \frac{x_i}{1 + x_{II} + x_{III}}.
\]

The values of \( w_i \) at 800 K were found to be as follows: for \( \text{Cs}_3\text{Br}_2^- \) are 0.77, 0.21 and 0.02; \( \text{Cs}_3\text{I}_2^- \) are 0.66, 0.27 and 0.07 and \( \text{Cs}_3\text{I}_3^- \) are 0.70, 0.24 and 0.06 that is of linear, cyclic and bipyramidal isomers, respectively. From these values, we can notice that the isomer I dominates for all ions, while the cyclic is less abundant but still significant in its amount, and the fraction of the bipyramidal does not exceed 10%. Fig. 5 elucidates the influence of temperature on the fraction of isomers \( w_i \). As it is seen raise in temperature increases the amount of linear isomer and decreases slowly that of cyclic isomers. For the bipyramid the fraction decreases rapidly as temperature elevates. Thus for all ions with temperature increase, the cyclic and bipyramidal isomers are decreasing in their content whereas isomer I is increasing and being predominant.

Concluding this section it is worth to emphasize the importance of the entropy factor on the relative content of the isomers. The effect of entropy and consequently in reduced Gibbs energy is appeared to be essential and prevailing over the energetic factor. In spite of the higher energetic stability of isomers II and III their relative amount is lower than of the isomer I. It is distinctly seen particularly for the bipyramidal isomer as its energy is lower by \(~30\) kJ mol\(^{-1}\) than that of the isomer I but its relative concentration is very small in saturated vapour at elevated temperatures. Therefore the considerable decrease in entropy of the isomerization reactions prevails over the energy factor and result in the predominance of the isomers I.

### 3.4 The Enthalpies of Dissociation Reactions and Enthalpies of Formation of Ions

In this section, we have examined the dissociation reactions of the cluster ions with elimination of CsX molecules. The energies of reactions \( \Delta E \) have been calculated at different theoretical levels, B3LYP5, MP2, MP2C, MP4, MP4C, where in MP2C and MP4C the BSSE correction have been taken into account. The results are presented in Fig. 6. One can see the similar trend in values of \( \Delta E \) with an enhancement of the theoretical level from B3LYP5 to MP4C i.e. the lowest values come from the B3LYP5 method, the highest ones from MP2 following by the further decreasing to the MP4C level. This trend is common either of tri- and pentaatomic ions. Also the distinct similarity may be observed for the same isomers of pentaatomic ions that is a slight oscillation of \( \Delta E \) from MP2 to MP4C for isomer I and almost monotonic decrease for both cyclic and bipyramidal isomers. From these results the true value of \( \Delta E \) comes when approaching the limit that we suppose is close to the MP4C result.
latter appeared to be an intermediate between B3LYP5 and MP2 results. Regarding a certain pentaatomic ion, the change in $\Delta E$ is not the same for different isomers that is the change in $\Delta E$ from MP2 to MP4C is about 10 kJ mol$^{-1}$ for the isomers I or II, while that is $\sim$20 kJ mol$^{-1}$ for the isomers III.

This results in a small decrease of the isomerization energies from MP2 to MP4 and further to MP4C. The BSSE correction itself looks slightly different for three isomers of the same ion; that contributes to the error of computational scheme [46] and hence to the uncertainties of the theoretical values of the enthalpies of the dissociation reactions accepted here.

The values of $\Delta E$ obtained using the MP4C level were taken for calculation of the enthalpies of the reactions $\Delta H^0(0)$ by Eq. (1). The results on $\Delta E$, $\Delta H^0(0)$, ZPVE, and $\Delta H^0(0)$ are listed in Table 8. The reference thermodynamic data required for the calculations of the enthalpies of formation $\Delta H^0(0)$ of the cluster ions were retrieved from [55]. The uncertainties of the theoretical values were estimated on the base of the results for the dimer molecules Cs$_2$X$_2$ (section 3.1).

Regarding the positive and negative triatomic ions with the same halogen, Cs$_2$Br$^+$ and CsBr$_2^-$ or CsJ$^+$ and CsJ$_2^-$, have nearly equal enthalpies of reaction respectively, while for the ions with different halogens the values for bromides are higher by 7–10 kJ mol$^{-1}$ than for iodides. For all ions, the decrease in enthalpies of dissociation is observed from tri- to pentaatomic ions, so triatomic ions are apparently more stable against decomposition than pentaatomic ions.

For the pentaatomic ions the dissociation reactions are considered for each of three isomers. Comparing the isomers of the same shape for the positive and negative ions with the same halogen, one can see that the enthalpies are very close to each other, e.g. for Cs$_2$Br$_2^+$ (I) and Cs$_2$Br$_2^-$ (I), $\Delta H^0(0) = 106$ and 108 kJ mol$^{-1}$, respectively or for Cs$_2$J$_2^+$ (III) and Cs$_2$J$_2^-$ (III), $\Delta H^0(0) = 124$ and 125 kJ mol$^{-1}$, respectively. The bigger difference is observed for the bipyramidal isomers of Cs$_2$Br$_2^+$ and Cs$_2$Br$_2^-$, 123 and 135 kJ mol$^{-1}$ which is probably due to the smaller size of Br than Cs atom and hence the bipyramidal Cs$_2$Br$_2^+$ ion with three Br atoms in the base has higher stability compared to Cs$_2$J$_2^+$ with three Cs atoms in the base.

Fig. 4. Temperature dependence of the relative amount of pentaatomic ions isomers $x_i = p_i/p_1$ where $i = II$ or III: (a) Cs$_3$Br$_2^+$; (b) Cs$_2$Br$_3^-$; (c) Cs$_3$I$_2^+$; (d) Cs$_2$I$_3^-$.
Fig. 5. The fractions $w_i$ ($i = I, II$ or III) of isomers versus temperature:
(a) $\text{Cs}_3\text{Br}_2^+$; (b) $\text{Cs}_3\text{I}_2^+$; (c) $\text{Cs}_2\text{I}_3^-$.
Comparing the bromides and corresponding iodides with the same shape and charge one can observe the higher values for bromides by 6–10 kJ·mol⁻¹, e.g. for Cs₂Br₂⁺ (I) and for Cs₂I₂⁺ (I), ∆₇H°(0) = 106 and 99 kJ·mol⁻¹, respectively or for Cs₃Br₂⁺ (III) and Cs₃I₂⁺ (III), ∆₇H°(0) = 135 and 125 kJ·mol⁻¹, respectively. The only one exclusion is observed for the enthalpies of dissociation of the bipyramidal ions Cs₂Br₂⁺ and Cs₂I₂⁻; 123 and 124 kJ·mol⁻¹, as no decrease...
from bromide to iodide is there. This result may be explained by a steric factor, the similar size of Cs and I atoms favours the Cs$_3$I$_2$$^-$ bipyramid compared to Cs$_3$Br$_2$$^-$ built of atoms of rather different size.

It is worth to remind here about the increase of stability of the isomers in the rank I–II–III; the enthalpy of dissociation of the isomer I is less by 6–11 kJ mol$^{-1}$ than of isomer II and 17–27 kJ mol$^{-1}$ compared to isomer III. The reason is that the isomers with compact shape are more stable against dissociation.

The experimental data are available in [24] for ions existing in vapour over cesium iodide where the ion molecular reactions were investigated by mass spectrometric method and the equilibrium constants $K_p^*$ for the heterophase reactions involving the tri- and pentaatomic cluster ions were measured. Using these constants we have computed the values of $\Delta_r H^r(0)$ by the formula:

$$ \Delta_r H^r(0 \ K) = -RT \ln K_p^* + T \Delta_r \Phi^r(T). $$ (6)

As an example, an ion molecular reaction for the positive triatomic ion may be expressed as follows:

$$ \text{CsI}^+ \rightarrow \text{[CsI]} + \text{Cs}^+. $$ (7)

where [CsI] corresponds to condensed phase. The equilibrium constant for this reaction is

$$ K_p^* = \frac{p(\text{Cs}^+)}{p(\text{CsI}^+)} = \frac{l(\text{Cs}^+)}{l(\text{CsI}^+)} \frac{m(\text{Cs}^+)}{m(\text{CsI}^+)} $$ (8)

where $l$ and $m$ are ion currents and molecular mass of the ions, respectively. The thermodynamic functions of the ions Cs$^+$ and I$^+$, and [CsI] were taken from [55]. The enthalpies of heterophase reactions were converted into enthalpies of gas phase reactions using the enthalpies of sublimation of CsI from [55]. The geometrical parameters and vibrational frequencies of the ions Cs$_3$I$_2$$^+$, Cs$_3$I$_2$$^-$, Cs$_3$Br$_2$$^+$, and Cs$_3$Br$_2$$^-$ needed for the calculation of the thermodynamic functions were taken from our MP2 results. The enthalpies of dissociation calculated through experimental data [24] are denoted as “based on experiment” hereafter and given in Table 8. As regards the pentaatomic ions, the existence of isomers had not been considered by Sidorova et al. [24]. In our work, as we have found the isomers may exist at a comparable amount, the fractions of the isomers, $w_i$ ($i = \text{I, II, or III}$), are taken into account, that is the measured current is multiplied by the fraction, e.g. the ion current for isomer I is $I(\text{Cs}_3\text{I}_2^+)$ = $I(\text{Cs}_3\text{I}_2^+)^{}w_1$. The values of the ion currents obtained by this way have been used to calculate the equilibrium constant for each isomer and then the enthalpies of reactions $\Delta_r H^r(0)$ “based on experiment”. It is worth to note that for the pentaatomic ions only a few values of currents had been measured and no statistical treatment was done in [24].

As is seen in Table 8, for the triatomic ions, Cs$_3$I$^+$ and Cs$_3$I$^-$, the theoretical magnitudes of $\Delta_r H^r(0)$ are in a good agreement with “based on experiment” values but underrated by ~5 kJ mol$^{-1}$. Similarly the theoretical values for the dimer molecules Cs$_3$Br$_2$ are underrated compared to experimental data which is mentioned above. For the pentaatomic isomers the agreement in most cases is worse than for triatomic ions and the discrepancy between theoretical values and “based on experiment” approaches 13 kJ mol$^{-1}$. In addition, while the theoretical results demonstrate almost equal energetic stability of the positive Cs$_3$Br$_2$$^+$ and negative Cs$_3$Br$_2$$^-$ ions of the same structure — 99 and 102 kJ mol$^{-1}$ for the

| Isomerization reaction | $\Delta_r E_{iso}$ (MP4), kJ mol$^{-1}$ | $\Delta r$ $\xi$, kJ mol$^{-1}$ | $\Delta_r H^r(0)$, kJ mol$^{-1}$ | $\Delta_r \Phi^r(T)$, J mol$^{-1}$ K$^{-1}$ | $x_i = p_i/p_0$ |
|------------------------|----------------------------------------|------------------------------|-----------------------------|----------------------------------------|-----------------|
| Cs$_3$Br$_2$$^+$ (I) = Cs$_3$Br$_2$$^-$ (II) | -5.4 | 0.32 | -5.1 | -17.4 | 0.27 |
| Cs$_3$Br$_2$$^+$ (I) = Cs$_3$Br$_2$$^-$ (III) | -21.6 | 0.96 | -20.6 | -54.8 | 0.03 |
| Cs$_3$Br$_3$$^+$ (I) = Cs$_3$Br$_3$$^-$ (II) | -9.2 | 0.60 | -8.6 | -43.2 | 0.02 |
| Cs$_3$Br$_3$$^+$ (I) = Cs$_3$Br$_3$$^-$ (III) | -33.2 | 1.21 | -32.0 | -83.4 | 0.005 |
| Cs$_3$I$_2$$^+$ (I) = Cs$_3$I$_2$$^-$ (II) | -5.8 | 0.32 | -5.4 | -14.5 | 0.40 |
| Cs$_3$I$_2$$^+$ (I) = Cs$_3$I$_2$$^-$ (III) | -27.7 | 0.74 | -26.9 | -52.1 | 0.11 |
| Cs$_3$I$_3$$^+$ (I) = Cs$_3$I$_3$$^-$ (II) | -7.0 | 0.39 | -6.6 | -17.0 | 0.35 |
| Cs$_3$I$_3$$^+$ (I) = Cs$_3$I$_3$$^-$ (III) | -28.5 | 0.82 | -27.7 | -54.8 | 0.09 |
Table 8. The dissociation reactions of the ions, energies $\Delta E$, enthalpies $\Delta H^\circ(0)$, and ZPVE corrections $\Delta \varepsilon$ of the reactions, and enthalpies of formation $\Delta fH^\circ(0)$ of the ions; all values are in kJ-mol$^{-1}$

| No | Reaction | $\Delta E$ | $\Delta \varepsilon$ | $\Delta H^\circ(0)$ Theoretical | $\Delta H^\circ(0)$ Based on expt$^a$ | $\Delta fH^\circ(0)$ Theoretical | $\Delta fH^\circ(0)$ Based on expt$^a$ |
|----|----------|------------|---------------------|--------------------------|----------------|---------------------|----------------|
| 1  | Cs$_2$Br$^+ = \text{CsBr} + \text{Cs}^+$ | 156.1 | −0.66 | 155±5 | 101±5 |
| 2  | CsBr$^+ = \text{Cs} + \text{CsBr}^-$ | 148.4 | −0.50 | 148±5 | −552±5 |
| 3  | CsI$^+ = \text{Cs} + \text{CsI}^-$ | 145.2 | −0.58 | 145±10 | 150±5 | 160±10 | 155±5 |
| 4  | Cs$_2$I$^+ = \text{CsI} + I^+$ | 141.7 | −0.46 | 141±10 | 146±5 | −478±10 | −483±5 |
| 5  | Cs$_2$Br$_2$ (I) = CsBr + Cs$_2$Br$^+$ | 106.3 | −0.65 | 106±10 | −202±10 |
| 6  | Cs$_2$Br$_2$ (II) = CsI + Cs$_2$Br$^+$ | 116.5 | −0.96 | 116±10 | −212±10 |
| 7  | Cs$_2$Br$_2$ (III) = Cs + Cs$_2$Br$^+$ | 124.8 | −1.60 | 124±10 | −219±10 |
| 8  | Cs$_2$Br$_3$ (I) = CsBr + CsBr$_2^-$ | 108.9 | −0.47 | 108±10 | −858±10 |
| 9  | Cs$_2$Br$_3$ (II) = CsBr + CsBr$_2^-$ | 115.6 | −0.47 | 115±10 | −864±10 |
| 10 | Cs$_2$Br$_3$ (III) = CsBr + CsBr$_2^-$ | 136.6 | −1.67 | 135±10 | −884±10 |
| 11 | Cs$_2$I$_2$ (I) = CsI + CsI$^-$ | 99.6 | −0.47 | 99±15 | −88±15 | −102±12 |
| 12 | Cs$_2$I$_2$ (II) = CsI + CsI$^-$ | 110.6 | −0.79 | 110±15 | −99±15 | −108±12 |
| 13 | Cs$_2$I$_2$ (III) = CsI + CsI$^-$ | 125.1 | −1.21 | 124±15 | −113±15 | −129±12 |
| 14 | Cs$_2$I$_3$ (I) = Cs + Cs$_2$I$^-$ | 102.6 | −0.48 | 102±15 | −729±15 | −746±12 |
| 15 | Cs$_2$I$_3$ (II) = CsI + Cs$_2$I$^-$ | 109.2 | −0.87 | 108±15 | −735±15 | −750±12 |
| 16 | Cs$_2$I$_3$ (III) = CsI + Cs$_2$I$^-$ | 126.6 | −1.30 | 125±15 | −757±15 | −770±12 |

The values $\Delta H^\circ(0)$ “based on experiment” were determined by us on the basis of the experimental equilibrium constants and geometrical parameters and vibrational frequencies of the ions. In the original work by Sidorova et al. [24], the enthalpies of the dissociation reactions (3) and (4) were 151.0 ± 5.4 and 151.4 ± 5.4 kJ-mol$^{-1}$, respectively. These values were found on the basis of the experimental equilibrium constants and estimated geometrical parameters and vibrational frequencies of the ions.

For the pentaatomic ions Cs$_2$X$_2^+$ and Cs$_2$X$_3^-$ different isomers of linear, planar cyclic, bipyramidal, and V-shaped were proved to exist in considerable fractions. The properties of the species with the similar structure look alike for positive and negative ions both in vibrational spectra and energetic stability. In spite of the highest energetic stability of the bipyramidal isomer its relative concentration is appeared to be small in saturated vapours at elevated temperatures.

Regarding the enthalpies of dissociation reactions of the dimer molecules and ions, $\Delta H^\circ(0)$, the DFT (B3LYP5 and B3P86) methods bring rather underrated values compared with experimental data available. The higher level of calculations MP4C allowed us to approach more reliable results and to come to better agreement with the literature data. Still as concerns cesium iodide species — the dimer molecule and ions — detailed analysis of the theoretical and experimental data shows that the experimental values of $\Delta H^\circ(0)$ seem to be somehow overrated and it would be desirable to refine them applying advanced experimental techniques.

4. CONCLUSION

The DFT (B3LYP5) and MP2 methods have been used to calculate geometrical parameters and vibrational frequencies of different cluster ions Cs$_2$X$^+$, Cs$_2$X$_2^+$, Cs$_2$X$^-$, and Cs$_2$X$_2^-$ (X = Br or I) existing in saturated vapours over cesium bromide and iodide. The results obtained by DFT and MP2 methods do not contradict each other and literature data as well. Nevertheless the MP2 method yields preferable results.
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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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APPENDIX

Thermodynamic Functions of the Cluster Ions

The thermodynamic functions of cluster ions \( \text{Cs}_2\text{X}^+, \text{CsX}_2^-, \text{Cs}_3\text{X}_2^+, \text{Cs}_2\text{X}_3^- \) (\( \text{X} = \text{Br}, \text{I} \)) used in calculations are given in Tables A1–A8 and B1–B8 for cesium bromide and cesium iodide, respectively; \( \Phi^\circ \) is the reduced Gibbs free energy; \( S^\circ \) is entropy; and \( H^\circ(T) - H^\circ(0) \) is the enthalpy increment. The values of \( \Phi^\circ \) and \( S^\circ \) are given in \( \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \), and \( H^\circ(T) - H^\circ(0) \) in \( \text{kJ} \cdot \text{mol}^{-1} \); absolute temperature \( T \) in kelvins.

### Table A1. Thermodynamic functions of \( \text{Cs}_2\text{Br}^+ \)

| \( T \)   | \( \Phi^\circ \) | \( S^\circ \) | \( H^\circ(T) - H^\circ(0) \) |
|-----------|-----------------|--------------|-----------------------------|
| 298.15    | 295.239         | 352.864      | 17.181                      |
| 700       | 345.678         | 405.922      | 41.171                      |
| 800       | 353.739         | 414.240      | 48.401                      |
| 900       | 360.877         | 421.579      | 54.631                      |
| 1000      | 376.282         | 428.145      | 60.863                      |
| 1100      | 373.089         | 434.085      | 67.096                      |
| 1200      | 378.401         | 439.508      | 73.329                      |
| 1300      | 383.296         | 444.498      | 79.563                      |
| 1400      | 387.835         | 449.118      | 85.796                      |
| 1500      | 392.065         | 453.419      | 92.031                      |
| 1600      | 396.027         | 457.442      | 98.265                      |

### Table A2. Thermodynamic functions of \( \text{CsBr}_2^- \)

| \( T \)   | \( \Phi^\circ \) | \( S^\circ \) | \( H^\circ(T) - H^\circ(0) \) |
|-----------|-----------------|--------------|-----------------------------|
| 298.15    | 297.551         | 355.651      | 17.323                      |
| 700       | 348.273         | 408.736      | 42.324                      |
| 800       | 356.363         | 417.056      | 48.555                      |
| 900       | 363.522         | 424.396      | 54.786                      |
| 1000      | 369.943         | 430.962      | 61.019                      |
| 1100      | 375.765         | 436.903      | 67.252                      |
| 1200      | 381.089         | 442.327      | 73.485                      |
| 1300      | 385.994         | 447.317      | 79.719                      |
| 1400      | 390.542         | 451.937      | 85.954                      |
| 1500      | 394.779         | 456.238      | 92.188                      |
| 1600      | 398.748         | 460.262      | 98.423                      |

### Table A3. Thermodynamic functions of \( \text{Cs}_3\text{Br}_2^+ \), isomer I (V-shaped)

| \( T \)   | \( \Phi^\circ \) | \( S^\circ \) | \( H^\circ(T) - H^\circ(0) \) |
|-----------|-----------------|--------------|-----------------------------|
| 298.15    | 435.304         | 533.967      | 29.416                      |
| 700       | 522.016         | 625.898      | 66.897                      |
| 800       | 535.923         | 640.315      | 76.862                      |
| 900       | 548.242         | 653.034      | 86.830                      |
| 1000      | 559.300         | 664.414      | 96.800                      |
| 1100      | 569.332         | 674.710      | 106.770                     |
| 1200      | 578.510         | 684.110      | 116.742                     |
| 1300      | 586.970         | 692.758      | 126.715                     |
| 1400      | 594.817         | 700.766      | 136.689                     |
| 1500      | 602.131         | 708.221      | 146.663                     |
| 1600      | 608.983         | 715.195      | 156.637                     |
| Table A4. Thermodynamic functions of Cs$_2$Br$_3^-$, isomer I (linear) |
|-------------|--------|--------|----------------|
| $T$ (K)   | $\Phi^\circ$ | $S^\circ$ | $H^\circ(T) - H^\circ(0)$ |
| 298.15    | 453.6812  | 557.533 | 30.963          |
| 700       | 544.552   | 653.058 | 75.954          |
| 800       | 559.072   | 668.032 | 87.168          |
| 900       | 571.926   | 681.242 | 98.384          |
| 1000      | 583.459   | 693.061 | 109.602         |
| 1100      | 593.917   | 703.754 | 120.821         |
| 1200      | 603.483   | 713.517 | 132.041         |
| 1300      | 612.296   | 722.498 | 143.262         |
| 1400      | 620.469   | 730.814 | 154.483         |
| 1500      | 628.087   | 738.556 | 165.704         |
| 1600      | 635.220   | 745.799 | 176.926         |

| Table A5. Thermodynamic functions of Cs$_2$Br$_2^-$, isomer II (cyclic) |
|-------------|--------|--------|----------------|
| $T$ (K)   | $\Phi^\circ$ | $S^\circ$ | $H^\circ(T) - H^\circ(0)$ |
| 298.15    | 418.579   | 516.190 | 29.103          |
| 700       | 504.685   | 608.116 | 3290.293        |
| 800       | 518.535   | 622.532 | 1388.692        |
| 900       | 530.811   | 635.252 | 842.065         |
| 1000      | 541.834   | 646.632 | 592.264         |
| 1100      | 551.836   | 656.927 | 451.532         |
| 1200      | 560.990   | 666.327 | 362.226         |
| 1300      | 569.430   | 674.975 | 300.905         |
| 1400      | 577.259   | 682.983 | 256.380         |
| 1500      | 584.559   | 690.438 | 222.694         |
| 1600      | 591.397   | 697.412 | 196.462         |

| Table A6. Thermodynamic functions of Cs$_2$Br$_3^-$, isomer II (cyclic) |
|-------------|--------|--------|----------------|
| $T$ (K)   | $\Phi^\circ$ | $S^\circ$ | $H^\circ(T) - H^\circ(0)$ |
| 298.15    | 415.791   | 513.565 | 29.151          |
| 700       | 501.997   | 605.507 | 72.457          |
| 800       | 515.857   | 619.924 | 83.254          |
| 900       | 528.141   | 632.644 | 94.053          |
| 1000      | 539.170   | 644.024 | 104.854         |
| 1100      | 549.177   | 654.320 | 115.657         |
| 1200      | 558.336   | 663.720 | 126.461         |
| 1300      | 566.780   | 672.368 | 137.265         |
| 1400      | 574.612   | 680.376 | 148.070         |
| 1500      | 581.914   | 687.831 | 158.876         |
| 1600      | 588.754   | 694.805 | 169.682         |

| Table A7. Thermodynamic functions of Cs$_3$Br$_2^+$, isomer III (bipyramidal) |
|-------------|--------|--------|----------------|
| $T$ (K)   | $\Phi^\circ$ | $S^\circ$ | $H^\circ(T) - H^\circ(0)$ |
| 298.15    | 382.493   | 478.083 | 28.500          |
| 700       | 467.417   | 569.957 | 71.778          |
| 800       | 481.156   | 584.371 | 82.572          |
| 900       | 493.344   | 597.098 | 93.369          |
| 1000      | 504.298   | 608.467 | 104.169         |
| 1100      | 514.244   | 618.762 | 114.970         |
| 1200      | 523.350   | 628.161 | 125.773         |
| 1300      | 531.750   | 636.808 | 136.576         |
| 1400      | 539.543   | 644.815 | 147.381         |
| 1500      | 546.813   | 652.270 | 158.185         |
| 1600      | 553.625   | 659.244 | 168.991         |
Table A. Thermodynamic functions of Cs$_2$Br$_3^-$, isomer III (bipyramidal)

| T     | $\Phi^\circ$ | $S^\circ$ | $H^\circ(T) - H^\circ(0)$ |
|-------|--------------|-----------|--------------------------|
| 298.150 | 376.844      | 472.659   | 28.567                   |
| 700    | 461.910      | 564.564   | 71.858                   |
| 800    | 475.663      | 578.979   | 82.653                   |
| 900    | 487.863      | 591.698   | 93.451                   |
| 1000   | 498.825      | 603.077   | 104.252                  |
| 1100   | 508.778      | 613.373   | 115.054                  |
| 1200   | 517.891      | 622.772   | 125.857                  |
| 1300   | 526.296      | 631.420   | 136.661                  |
| 1400   | 534.095      | 639.427   | 147.465                  |
| 1500   | 541.368      | 646.882   | 158.271                  |
| 1600   | 548.184      | 653.856   | 169.076                  |

Table B. Thermodynamic functions of Cs$_2$I$^+$

| T     | $\Phi^\circ$ | $S^\circ$ | $H^\circ(T) - H^\circ(0)$ |
|-------|--------------|-----------|--------------------------|
| 298.15 | 303.678      | 362.052   | 17.405                   |
| 700    | 354.570      | 415.166   | 42.417                   |
| 800    | 362.676      | 423.487   | 48.649                   |
| 900    | 369.848      | 430.827   | 54.881                   |
| 1000   | 376.280      | 437.395   | 61.115                   |
| 1100   | 382.110      | 443.336   | 67.348                   |
| 1200   | 387.442      | 448.760   | 73.582                   |
| 1300   | 392.353      | 453.750   | 79.817                   |
| 1400   | 396.906      | 458.371   | 86.051                   |
| 1500   | 401.148      | 462.672   | 92.286                   |
| 1600   | 405.121      | 466.696   | 98.521                   |

Table B. Thermodynamic functions of CsI$_2^-$

| T     | $\Phi^\circ$ | $S^\circ$ | $H^\circ(T) - H^\circ(0)$ |
|-------|--------------|-----------|--------------------------|
| 298.15 | 309.246      | 368.052   | 17.533                   |
| 700    | 354.570      | 415.166   | 42.417                   |
| 800    | 362.676      | 423.487   | 48.649                   |
| 900    | 369.848      | 430.827   | 54.881                   |
| 1000   | 376.280      | 437.395   | 61.115                   |
| 1100   | 382.110      | 443.336   | 67.348                   |
| 1200   | 387.442      | 448.760   | 73.582                   |
| 1300   | 392.353      | 453.750   | 79.817                   |
| 1400   | 396.906      | 458.371   | 86.051                   |
| 1500   | 401.148      | 462.672   | 92.286                   |
| 1600   | 405.121      | 466.696   | 98.521                   |

Table B. Thermodynamic functions of Cs$_3$I$_2^+$, isomer I (linear)

| T     | $\Phi^\circ$ | $S^\circ$ | $H^\circ(T) - H^\circ(0)$ |
|-------|--------------|-----------|--------------------------|
| 298.15 | 446.083      | 550.685   | 31.187                   |
| 700    | 537.413      | 646.280   | 76.207                   |
| 800    | 551.977      | 661.257   | 87.424                   |
| 900    | 564.868      | 674.470   | 98.642                   |
| 1000   | 576.429      | 686.291   | 109.862                  |
| 1100   | 586.911      | 696.986   | 121.082                  |
| 1200   | 596.497      | 706.749   | 132.303                  |
| 1300   | 605.327      | 715.731   | 143.525                  |
| 1400   | 613.514      | 724.048   | 154.747                  |
| 1500   | 621.145      | 731.791   | 165.969                  |
| 1600   | 628.288      | 739.033   | 177.192                  |
Table B4. Thermodynamic functions of Cs$_2$I$_3^-$, isomer I (linear)

| $T$  | $\Phi^\circ$  | $S^\circ$  | $H^\circ(T) - H^\circ(0)$ |
|------|---------------|------------|--------------------------|
| 298.15 | 445.83 | 550.755 | 31.283 |
| 700    | 537.355 | 646.374 | 76.313 |
| 800    | 551.940 | 661.353 | 87.531 |
| 900    | 564.845 | 674.567 | 98.750 |
| 1000   | 576.418 | 686.388 | 109.970 |
| 1100   | 586.909 | 697.083 | 121.191 |
| 1200   | 596.504 | 706.847 | 132.412 |
| 1300   | 605.541 | 715.829 | 143.634 |
| 1400   | 613.534 | 724.146 | 154.857 |
| 1500   | 621.170 | 731.889 | 166.079 |
| 1600   | 628.318 | 739.132 | 177.302 |

Table B5. Thermodynamic functions of Cs$_3$I$_2^+$, isomer II (cyclic)

| $T$  | $\Phi^\circ$  | $S^\circ$  | $H^\circ(T) - H^\circ(0)$ |
|------|---------------|------------|--------------------------|
| 298.15 | 428.610 | 528.018 | 29.638 |
| 700    | 515.792 | 620.054 | 72.983 |
| 800    | 529.746 | 634.476 | 83.784 |
| 900    | 542.103 | 647.199 | 94.586 |
| 1000   | 553.192 | 658.582 | 105.390 |
| 1100   | 563.248 | 668.879 | 116.194 |
| 1200   | 572.448 | 678.281 | 127.000 |
| 1300   | 580.926 | 686.930 | 137.805 |
| 1400   | 588.788 | 694.939 | 148.612 |
| 1500   | 596.115 | 702.394 | 159.418 |
| 1600   | 602.978 | 709.369 | 170.225 |

Table B6. Thermodynamic functions of Cs$_2$I$_3^-$, isomer II (cyclic)

| $T$  | $\Phi^\circ$  | $S^\circ$  | $H^\circ(T) - H^\circ(0)$ |
|------|---------------|------------|--------------------------|
| 298.15 | 438.302 | 537.833 | 29.675 |
| 700    | 525.557 | 629.876 | 73.023 |
| 800    | 539.519 | 644.299 | 83.824 |
| 900    | 551.882 | 658.582 | 94.626 |
| 1000   | 562.975 | 668.405 | 105.430 |
| 1100   | 573.035 | 678.703 | 116.235 |
| 1200   | 582.238 | 688.105 | 127.040 |
| 1300   | 590.926 | 696.754 | 137.846 |
| 1400   | 598.788 | 704.762 | 148.652 |
| 1500   | 605.912 | 712.218 | 159.459 |
| 1600   | 612.777 | 719.193 | 170.266 |

Table B7. Thermodynamic functions of Cs$_3$I$_2^+$, isomer III (bipyramidal)

| $T$  | $\Phi^\circ$  | $S^\circ$  | $H^\circ(T) - H^\circ(0)$ |
|------|---------------|------------|--------------------------|
| 298.15 | 391.065 | 489.077 | 29.222 |
| 700    | 486.032 | 589.692 | 72.562 |
| 800    | 499.910 | 604.113 | 83.362 |
| 900    | 512.209 | 616.836 | 94.164 |
| 1000   | 523.251 | 628.219 | 104.968 |
| 1100   | 533.269 | 638.516 | 115.772 |
| 1200   | 542.437 | 647.918 | 126.577 |
| 1300   | 550.889 | 656.567 | 137.382 |
| 1400   | 558.726 | 664.575 | 148.189 |
| 1500   | 566.034 | 672.031 | 158.995 |
| 1600   | 572.879 | 679.005 | 169.802 |
Table B8. Thermodynamic functions of Cs$_2$I$_3^-$, isomer III (bipyramidal)

| $T$  | $\Phi^\circ$ | $S^\circ$ | $H^\circ(T) - H^\circ(0)$ |
|------|--------------|-----------|-------------------------|
| 298.15 | 401.919 | 500.054 | 29.259 |
| 700  | 488.365 | 592.077 | 72.599 |
| 800  | 502.251 | 606.499 | 83.399 |
| 900  | 514.554 | 619.221 | 94.200 |
| 1000 | 525.600 | 630.604 | 105.004 |
| 1100 | 535.621 | 640.901 | 115.808 |
| 1200 | 544.792 | 650.303 | 126.613 |
| 1300 | 553.245 | 658.952 | 137.419 |
| 1400 | 561.085 | 666.960 | 148.225 |
| 1500 | 568.395 | 674.416 | 159.031 |
| 1600 | 575.241 | 681.390 | 169.838 |

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