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Molecular structures and thermodynamic properties of 12 gaseous cesium-containing species of nuclear safety interest: Cs_2 , CsH , CsO , Cs_2O , CsX , and Cs_2X_2 ($\text{X} = \text{OH}$, Cl , Br , and I)

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ABSTRACT

Ab initio electronic structure calculations at the coupled cluster level with a correction for the triples extrapolated to the complete basis set limit have been made for the estimation of the thermochemical properties of Cs_2 , CsH , CsO , Cs_2O , CsX , and Cs_2X_2 ($\text{X} = \text{OH}$, Cl , Br , and I). The standard enthalpies of formation and standard molar entropies at 298 K, and the temperature dependence of the heat capacities at constant pressure were evaluated. The calculated thermochemical properties are in good agreement with their literature counterparts. For Cs_2 , CsH , CsOH , $\text{Cs}_2(\text{OH})_2$, CsCl , Cs_2Cl_2 , CsBr , CsI , and Cs_2I_2 , the calculated $\Delta_f H_{298\text{K}}^\circ$ values are within chemical accuracy of the most recent experimental values. Based on the excellent agreement observed between our calculated $\Delta_f H_{298\text{K}}^\circ$ values and their literature counterparts, the standard enthalpies of formation at 298 K are estimated to be the following: $\Delta_f H_{298\text{K}}^\circ (\text{CsO}) = 17.0 \text{ kJ mol}^{-1}$ and $\Delta_f H_{298\text{K}}^\circ (\text{Cs}_2\text{Br}_2) = -575.4 \text{ kJ mol}^{-1}$.

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1. Introduction

Evaluation of the behavior of fission products, that can be released from the damaged fuel and transported through the reactor coolant system to the reactor containment, is a key safety issue of nuclear Pressurized Water Reactor (PWR). Among these fission products, iodine and cesium, which can be released and transported outside in the case of the containment building leakages, are of particular interest due to their high radiotoxicities at short term for iodine and at middle term for cesium. The French Institut de Radioprotection et de Sûreté Nucléaire (IRSN) [1] has undertaken programs combining experimental and theoretical efforts in order to reduce the rather large uncertainties of the fission products behavior in case of severe accident scenarios on PWR.

This paper is the third of a series [2,3] devoted to a better understanding of the chemical speciation along the transport of fission products in the reactor coolant system (RCS) in order to estimate the Source Term in case of a nuclear power plant accident. Cesium

is well known to be very reactive with iodine [4]. As reported in the literatures [5,6], almost all iodine is emitted in the containment under aerosol form corresponding to monomer or dimer cesium iodide. The gas-phase reaction kinetics [7] have been modeled for the release of cesium and iodine into steam and steam/hydrogen atmospheres following some postulated loss-of-coolant accidents. A total of seventeen chemical species were used in the model including all important cesium and iodine species: Cs atom and its dimer Cs_2 , CsH , CsO , Cs_2O , CsOH , $\text{Cs}_2(\text{OH})_2$, CsI , and Cs_2I_2 . In addition, other halogens present in the RCS (noticeably Cl and Br) can react with cesium in a similar way that iodine does. The following species have been therefore added to the set of species of interest: CsCl , CsBr , and their dimers (Cs_2Cl_2 and Cs_2Br_2). The standard enthalpy of formation at 298 K, $\Delta_f H_{298\text{K}}^\circ$, for the 12 studied species has been chosen as the main criterion to determine the suitable theoretical methodology able to predict the thermochemical properties ($\Delta_f H_{298\text{K}}^\circ$, $S_{298\text{K}}^\circ$, $C_p = f(T)$) for the cesium compounds of safety nuclear interest.

A selection of literature data concerning the molecular properties (geometric parameters and vibrational frequencies) and the thermochemical properties ($\Delta_f H_{298\text{K}}^\circ$, $S_{298\text{K}}^\circ$, $C_p = f(T)$) for the 12 Cs-containing species has been collected in Tables 1 and 2. These data were taken from literature reviews and evaluations (NIST-JANAF [8], NIST-Webbook [9], Cordfunke and Konings [10], Gurvich et al. [11], Thermodata database [12,13], SGTE database [14], and Glushko et al. [15]). Molecular parameters for the CsO radical have

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Table 1

Literature data – geometric parameters and vibrational frequencies for Cs-containing species.

Species	Geometric parameters	Method	Reference
Cs ₂	$r(\text{Cs}–\text{Cs}) = 4.646 \text{ \AA}$	Experimental ^a	NIST-JANAF [8]
CsH	$r(\text{Cs}–\text{H}) = 2.494 \text{ \AA}$	Estimation	NIST-Webbook [9]
CsO	$r(\text{Cs}–\text{O}) = 2.40 \text{ \AA}$ $r(\text{Cs}–\text{O}) = 2.39 \text{ \AA}$ $r(\text{Cs}–\text{O}) = 2.30 \text{ \AA}$	Estimation Estimation Experimental ^b	NIST-JANAF [8] Cordfunke and Konings [10] Yamada and Hirota [16]
Cs ₂ O	$r(\text{Cs}–\text{O}) = 2.4 \text{ \AA}$, $\theta = 105^\circ$ $r(\text{Cs}–\text{O}) = 2.28 \text{ \AA}$, $\theta = 140^\circ$	Estimation Estimation for r , Experimental ^c for θ	NIST-JANAF [8] Cordfunke and Konings [10]
CsOH	$r(\text{Cs}–\text{O}) = 2.391 \text{ \AA}$, $r(\text{O}–\text{H}) = 0.96 \text{ \AA}$, $\theta = 180^\circ$ $r(\text{Cs}–\text{O}) = 2.395 \text{ \AA}$, $r(\text{O}–\text{H}) = 0.92 \text{ \AA}$, $\theta = 180^\circ$ $r(\text{Cs}–\text{O}) = 2.403 \text{ \AA}$, $r(\text{O}–\text{H}) = 0.920 \text{ \AA}$, $\theta = 180^\circ$	Experimental ^b for $r(\text{Cs}–\text{O})$ and θ , estimation for $r(\text{O}–\text{H})$ Experimental ^b Experimental ^b	NIST-JANAF [8] Cordfunke and Konings [10] Gurvich et al. [11]
Cs ₂ (OH) ₂	$r(\text{Cs}–\text{O}) = 2.63 \text{ \AA}$, $r(\text{O}–\text{H}) = 0.96 \text{ \AA}$, $\theta(\text{CsOCs}) = 90^\circ$, $\theta(\text{CsOH}) = 110^\circ$ $r(\text{Cs}–\text{O}) = 2.61 \text{ \AA}$, $r(\text{O}–\text{H}) = 0.97 \text{ \AA}$, $\theta(\text{CsOCs}) = 92^\circ$ $r(\text{Cs}–\text{O}) = 2.60 \text{ \AA}$, $r(\text{O}–\text{H}) = 0.97 \text{ \AA}$, $\theta(\text{CsOCs}) = 90^\circ$	Estimation Model Estimation	NIST-JANAF [8] Cordfunke and Konings [10] Gurvich et al. [11]
CsCl	$r(\text{Cs}–\text{Cl}) = 2.906 \text{ \AA}$	Experimental ^b	NIST-JANAF [8]
Cs ₂ Cl ₂	$r(\text{Cs}–\text{Cl}) = 3.18 \text{ \AA}$, $\theta(\text{ClCsCl}) = 93.2^\circ$	Estimation	NIST-JANAF [8]
CsBr	$r(\text{Cs}–\text{Br}) = 3.072 \text{ \AA}$ $r(\text{Cs}–\text{Br}) = 3.099 \text{ \AA}$	Experimental ^b Experimental ^d	NIST-Webbook [9] Hartley and Fink [18]
Cs ₂ Br ₂	$r(\text{Cs}–\text{Br}) = 3.356 \text{ \AA}$, $\theta(\text{BrCsBr}) = 85^\circ$	Experimental ^d	Hartley and Fink [18]
CsI	$r(\text{Cs}–\text{I}) = 3.315 \text{ \AA}$ $r(\text{Cs}–\text{I}) = 3.314 \text{ \AA}$	Experimental ^b Experimental ^d	NIST-Webbook [9] Hartley and Fink [22]
Cs ₂ I ₂	$r(\text{Cs}–\text{I}) = 3.572 \text{ \AA}$, $\theta(\text{CsICs}) = 96.5^\circ$	Experimental ^e	Cordfunke and Konings [10]
Vibrational frequencies ^f (cm ^{−1})			
Cs ₂	42	Experimental ^g	NIST-JANAF [8]
CsH	891	Estimation	NIST-Webbook [9]
CsO	280 314 357	Estimation Experimental ^h Experimental ⁱ	NIST-JANAF [8] Cordfunke and Konings [10] Yamada and Hirota [16]
Cs ₂ O	130, 290, 300 60, 305, 455	Estimation Estimation for ν_1 , ν_2 ; Experimental ^h for ν_3	NIST-JANAF [8] Cordfunke and Konings [10]
CsOH	306, 306, 336, 3610 306, 306, 336, 3700 306, 306, 336, 3705 320, 320, 360	Experimental ^j for ν_1 , ν_2 ; estimation for ν_3 Experimental ^j Experimental ^j Experimental ^k	NIST-JANAF [8] Cordfunke and Konings [10] Gurvich et al. [11] Konings et al. [17]
Cs ₂ (OH) ₂	110, 120, 200, 210, 220, 230, 1250, 1250, 1250, 1250, 3700, 3700 86, 113, 185, 227, 235, 272, 275, 275, 278, 281, 3700, 3700 85, 113, 185, 227, 235, 272, 275, 275, 279, 280, 3700, 3700 230	Estimation Experimental ^j and estimation Experimental ^j and estimation Experimental ^k (Cs–O stretch)	NIST-JANAF [8] Cordfunke and Konings [10] Gurvich et al. [11] Konings et al. [17]
CsCl	213	Experimental ⁱ	NIST-JANAF [8]
Cs ₂ Cl ₂	67, 76, 140, 141, 151, 156	Model	NIST-JANAF [8]
CsBr	150 150 141	Experimental ^l Experimental ^m Experimental ⁿ	NIST-Webbook [9] Hartley and Fink [18] Groen and Kovács [21]
Cs ₂ Br ₂	108, 110	Experimental ⁿ	Groen and Kovács [21]
CsI	119 119 117	Experimental ^l Experimental ^m Experimental ⁿ	NIST-Webbook [9] Hartley and Fink [22] Groen and Kovács [21]
Cs ₂ I ₂	25, 44, 62, 82, 89, 90 29 88, 95	Model Experimental ^k Experimental ⁿ	Cordfunke and Konings [10] Konings et al. [23] Groen and Kovács [21]

^a Fluorescence spectra.^b Microwave spectrum.^c IR matrix isolation study (N₂).^d Electron diffraction study.^e IR spectroscopy.^f Values in italics correspond to the selected experimental frequencies for the calculation of the scaling factor.^g Fluorescence spectra.^h IR matrix isolation study (N₂).ⁱ Microwave spectrum.^j IR matrix isolation study (Ar).^k IR spectroscopy.^l Derived from rotational constants.^m Electron diffraction study.ⁿ IR matrix isolation studies (Kr, Xe).

been derived from a microwave study by Yamada and Hirota [16]. Konings et al. [17] reported experimental vibrational frequencies

for CsOH and its dimer Cs₂(OH)₂ from their high-temperature vibration spectrum. Hartley and Fink derived the molecular

Table 2

Literature data – thermochemical properties for Cs-containing species.

Species	$\Delta_f H_{298K}^\circ$ (kJ mol ⁻¹)	S_{298K}° (J mol ⁻¹ K ⁻¹)	$C_{p,298}$ (J mol ⁻¹ K ⁻¹)	Reference
Cs ₂	107.37 ± 0.30	284.675 ± 0.084	38.250	NIST-JANAF [8]
	109.4 ± 2.0	284.569	38.256	Cordfunke and Konings [10]
	109.405	284.569	38.239	Thermodata database [12,13]
CsH	116.859	214.949	31.472	Thermodata database [12,13]
	115.949	215.071	31.548	SGTE database [14]
CsO	62.8 ± 41.8	225.5 ± 4.2	36.481	NIST-JANAF [8]
	38.2 ± 10.0	248.665	37.520	Cordfunke and Konings [10]
Cs ₂ O	-92.0 ± 41.8	318.1 ± 8.4	55.388	NIST-JANAF [8]
	-159 ± 25	319.887	54.126	Cordfunke and Konings [10]
	-142.862	324.018	55.390	Thermodata database [12,13]
CsOH	-259.4 ± 12.6	254.78 ± 0.42	49.723	NIST-JANAF [8]
	-257.0 ± 3.0	254.681	49.721	Cordfunke and Konings [10]
	-256.0 ± 5	255.147 ^a	49.771 ^a	Gurvich et al. [11]
	-252.7 ± 4.1			Roki et al. [19–20]
Cs ₂ (OH) ₂	-687.8 ± 41.8	360.7 ± 12.6	82.807	NIST-JANAF [8]
	-642.0 ± 5.0	380.892	108.286	Cordfunke and Konings [10]
	-653.0 ± 8	381.937 ^a	108.385 ^a	Gurvich et al. [11]
	-652.4 ± 11.7			Roki et al. [19–20]
CsCl	-240.16 ± 4.2	256.070 ± 0.021	36.952	NIST-JANAF [8]
	-240.162	255.956	36.953	Thermodata database [12,13]
Cs ₂ Cl ₂	-659.82 ± 10.5	383.445 ± 8.4	81.617	NIST-JANAF [8]
	-659.817	383.254	82.281	Thermodata database [12,13]
	-644.658	384.468	83.142	SGTE database [14]
CsBr	-209.200	267.316	37.070	Thermodata database [12,13]
Cs ₂ Br ₂	-565.829	413.791	82.436	SGTE database [14]
CsI	-154.3 ± 2.1	275.174	37.428	Cordfunke and Konings [10]
	-154.960	271.377	37.335	Thermodata database [12,13]
	-152.32 ± 3	275.283	37.419	Glushko et al. [15]
	-153.27 ± 4.2			Roki [20]
Cs ₂ I ₂	-464.3 ± 5.1	431.291	82.677	Cordfunke and Konings [10]
	-466.380	431.080	82.678	Thermodata database [12,13]
	-470.56 ± 10	431.181	82.676	Glushko et al. [15]
				Roki [20]

^a Values estimated at 300 K.

parameters for CsBr and Cs₂Br₂ from their gas electron diffraction study [18]. Based on high temperature mass spectrometric measurements, Roki et al. [19,20] estimated the standard enthalpies of formation at 298 K for CsOH, Cs₂(OH)₂, CsI, and Cs₂I₂. Groen and Kovács [21] derived the vibrational frequencies from a matrix-isolation FTIR study for CsBr, Cs₂Br₂, CsI, and Cs₂I₂ while Hartley and Fink provided molecular parameters for CsI [22]. Konings et al. reported two vibrational frequencies for the Cs₂I₂ dimer in their high-temperature infrared study of the vaporization of CsI [23].

The corresponding $\Delta_f H_{298K}^\circ$ values are also reported in Table 2. The examination of Table 2 shows that there are still large uncertainties associated with the standard enthalpies of formation at 298 K mainly for cesium oxides (CsO and Cs₂O) as well as for cesium hydroxides (CsOH and Cs₂(OH)₂).

In this work, highly correlated ab initio quantum chemistry calculations are performed to compute molecular parameters and thermochemical properties for 12 cesium compounds of safety nuclear interest. A wide variety of levels of theory, described hereafter, have been used in the objective to select the most reliable methods able to compute accurately the thermochemistry of the cesium-containing compounds. The use of this computational methodology will be extended in a next step to the estimation of kinetic parameters for elementary reactions involving cesium-containing species.

This article is organized as follows: computational methods are reported in Section 2, while the results are presented and discussed in Section 3.

2. Computational methods

All calculations were performed using the GAUSSIAN03 software package [24]. Geometric parameters were fully optimized with the MP2 method [25]. Two different basis sets and effective core potentials (ECP) were employed in this work for the cesium atom: ECP46MDF[8s,8p,5d,3f,2g] [26] and ECP46MWB[10s,8p,5d,4f,3g] [27,28]. For clarity purposes, these two basis sets and effective core potentials are denoted throughout this paper ECP46MDF and ECP46MWB, respectively. The influence of the basis set size on the other elements (H, O, Cl, Br, and I) was also considered in this study. The H, O, Cl, and Br atoms were described by two different Dunning's correlation consistent basis sets [29–33] (cc-pVTZ and aug-cc-pVTZ). For the iodine atom, we used the cc-pVTZ-PP and aug-cc-pVTZ-PP basis sets of Peterson et al. [34], which incorporate a small-core (28MDF) relativistic potential that largely accounts for scalar relativistic effects in iodine (these basis sets will be written without the PP term throughout the paper). Scaled vibrational frequencies and scaled Zero-Point Energies (ZPEs) were determined within the harmonic approximation at the same level of theory as that for geometries. The ab initio vibrational frequencies for all cesium-containing species were multiplied by an appropriate scaling factor, which was obtained at each level of theory by plotting experimental frequencies for Cs₂, CsO, Cs₂O, CsOH, Cs₂(OH)₂, CsCl, CsBr, Cs₂Br₂, CsI, and Cs₂I₂ (see values in italics in Table 1) versus calculated frequencies. The calculated values are 0.957, 0.958, 0.955, and 0.957 at the MP2/cc-pVTZ + ECP46MDF, MP2/aug-cc-pVTZ + ECP46MDF, MP2/cc-pVTZ + ECP46MWB, and MP2/

aug-cc-pVTZ + ECP46MWB levels of theory, respectively (The ECP46MDF and ECP46MWB correspond to the two different basis sets and effective core potentials for the cesium atom).

The stability of the wavefunction was systematically checked using the algorithm implemented [35–37] in the GAUSSIAN03 software package [24]. In case of either an internal instability or a RHF → UHF instability, the wavefunction was re-optimized in order to obtain geometries with a stable wavefunction. Such procedure has been mainly applied to the cesium dimer with the MP2 method.

Thus, electronic energies were obtained employing the single and double coupled cluster theory with inclusion of a perturbative estimation for triple excitation (CCSD(T)) [38–42] with the aug-cc-pVnZ ($n = T, Q, 5$) basis sets (the frozen-core approximation has been applied in CCSD(T) calculations, which implies that the inner shells are excluded at estimating the correlation energy). The CCSD(T) calculated potential energies were extrapolated to the complete basis limit (CBS) using the relation of Halkier et al. [43]

$$E(\text{CBS}/\text{Halkier}) = \frac{5^3 E_{\text{a5Z}} - 4^3 E_{\text{aQZ}}}{5^3 - 4^3} \quad (2-1)$$

where aQZ and a5Z correspond to the CCSD(T)/aug-cc-pVQZ and CCSD(T)/aug-cc-pV5Z levels of theory, respectively. The CCSD(T) total energies were also extrapolated to the CBS limit using a mixed exponential/Gaussian function of the form as first proposed by Peterson et al. [32]

$$E(n) = E(\text{CBS}/\text{Peterson}) + A \exp(-(n-1)) + B \exp(-(n-1)^2) \quad (2-2)$$

with $n = 3$ (aTZ), 4 (aQZ), and 5 (a5Z).

In order to estimate the basis set superposition error (BSSE) in the Cs_2X_2 species ($X = \text{OH}, \text{Cl}, \text{Br}, \text{and I}$), the counterpoise correction [44,45] has been applied at the twenty different levels of theory.

Spin-orbit coupling is of crucial importance, especially in the case of halogen atoms [46,47]. The values of the spin-orbit corrections to the calculated potential energies for O (^3P) [48], Cl ($^2\text{P}_{3/2}$) [48], Br ($^2\text{P}_{3/2}$) [48], I ($^2\text{P}_{3/2}$) [48], OH [49], HBr [50], HI [50], and CsO [51] are collected in Table 3. The molecular spin-orbit correction in CsI has been taken to two-third of the splitting in the I atom as previously reported by Berkowitz et al. [52] in their work on photoelectron spectra of high-temperature vapors. By analogy to CsI, the spin-orbit corrections for CsCl and CsBr compounds have been also estimated to two-third of those in the Cl and Br atoms, respectively. In the case of the Cs_2X_2 species ($X = \text{Cl}, \text{Br}, \text{and I}$), the spin-orbit corrections are estimated to be about two times greater than the ones found in the monomer CsX.

Table 3
Spin-orbit corrections to the calculated potential energies for the species involved in this work.

Species	Spin-orbit correction (kJ mol ⁻¹)	Reference
O (^3P)	−0.93	Moore [48]
Cl ($^2\text{P}_{3/2}$)	−3.51	Moore [48]
Br ($^2\text{P}_{3/2}$)	−14.69	Moore [48]
I ($^2\text{P}_{3/2}$)	−30.29	Moore [48]
OH	−0.83	Johnson [49]
HBr	−0.42	Feller et al. [50]
HI	−2.09	Feller et al. [50]
CsO	−1.2	Hirota [51]
CsCl	−2.34	
Cs ₂ Cl ₂	−4.68	
CsBr	−9.80	
Cs ₂ Br ₂	−19.60	
CsI	−20.19	
Cs ₂ I ₂	−40.38	

3. Results and discussion

3.1. Geometric parameters and vibrational frequencies

Tables 4 and 5 gather the optimized geometry parameters and scaled vibrational frequencies for Cs_2 , CsH, CsO, Cs_2O , CsOH, $\text{Cs}_2(\text{OH})_2$, CsCl, Cs_2Cl_2 , CsBr, Cs_2Br_2 , CsI, and Cs_2I_2 calculated at the MP2/cc-pVTZ and MP2/aug-cc-pVTZ levels of theory with the two different basis sets for cesium (ECP46MDF and ECP46MWB). As shown in Table 4, there is slight influence on the calculated bond lengths, bond angles and dihedral angles when increasing the basis set size, either from cc-pVTZ to aug-cc-pVTZ, or from ECP46MDF to ECP46MWB. A good agreement is almost observed between the calculated geometric parameters and the literature values which are gathered in Table 1. There are however more important differences for the bond angles $\theta(\text{CsOCs})$ in Cs_2O and $\theta(\text{CsOH})$ in $\text{Cs}_2(\text{OH})_2$. For Cs_2O , Cordfunke and Konings [10] reported a value of 140° for the bond angle $\theta(\text{CsOCs})$, which was derived from a N_2 -matrix study [53]. The value of 105° from the NIST-JANAF database [8] corresponds to a crude estimation by analogy to the water molecule. Unfortunately, some matrix effects can be expected as observed for the CsO species leading to large uncertainties in the 140° value. Our calculations predict a linear structure at all levels of theory. The same results for Cs_2O have been obtained previously by Burk and Tamp [54] in their theoretical study about the gas-phase basicities and proton affinities of alkali metal oxides. Chase [8] estimated the bond angle $\theta(\text{CsOH})$ in $\text{Cs}_2(\text{OH})_2$ by comparison with related molecules including CsOH, Cs_2F_2 , and H_2O . Our calculated values correspond however to a D_{2h} configuration which is in agreement with the other literature data [10,11].

The calculated scaled vibrational frequencies for the 12 cesium-containing species are in reasonable agreement with their literature counterparts. For the diatomic species (CsH, CsCl, CsBr, and CsI), there are very small differences between calculated scaled harmonic vibrational frequencies and literature values with the exception of the Cs_2 molecule where all levels of theory underestimate the vibrational frequency by about 17%. In the case of the CsO radical, our calculated values ($361, 351, 341$, and 340 cm^{-1} at the MP2/cc-pVTZ + ECP46MDF, MP2/aug-cc-pVTZ + ECP46MDF, MP2/cc-pVTZ + ECP46MWB, and MP2/aug-cc-pVTZ + ECP46MWB levels of theory, respectively) are in excellent agreement with the 357 cm^{-1} derived from the microwave spectrum study of CsO by Yamada and Hirota [16]. The difference observed between our calculated values and the frequency from a matrix-IR study [10] (differing by 43 cm^{-1} from the former accurate experimental value) is far more important. It could be noticed that the latter frequency suffers from matrix effects. The calculated scaled values for the antisymmetric-stretching mode of Cs_2O are ranging from 450 to 456 cm^{-1} depending on the level of theory. These values are apparently very close to the experimental frequency taken from the N_2 -matrix study (455 cm^{-1}) by Spiker and Andrews [53]. In the reality, this value may be in error by 40 – 50 cm^{-1} , if the matrix effect is the same as for the CsO radical. It could be noticed that our calculated vibrational frequencies for the CsOCs bending mode (about 68 cm^{-1} at all levels of theory) are close to the value of 60 cm^{-1} estimated by Lamoreaux and Hildebrand [55]. Two vibrational bands of CsOH (320 and 360 cm^{-1}) and one vibrational band of its dimer $\text{Cs}_2(\text{OH})_2$ (230 cm^{-1}) were determined by high-temperature infrared spectroscopy [17]. These values for the monomer and dimer again reasonably agree with our results. Two vibrational bands of Cs_2I_2 (29 and 76 cm^{-1}) were reported by Konings et al. [23]. These values are in good agreement with our calculations. For the ground states of CsOH, $\text{Cs}_2(\text{OH})_2$, Cs_2Cl_2 , and Cs_2I_2 , the calculated lowest vibrational modes (ν_1, ν_2, ν_3) exhibit the largest

Table 4Optimized geometry parameters^a calculated at different levels of theory.

Species	Parameters	Level of theory			
		MP2/ECP46MDF		MP2/ECP46MWB	
Cs ₂	$r(\text{Cs}-\text{Cs})$	4.749		4.742	
		MP2/cc-pVTZ		MP2/aug-cc-pVTZ	
		ECP46MDF	ECP46MWB	ECP46MDF	ECP46MWB
CsH	$r(\text{Cs}-\text{H})$	2.476	2.480	2.485	2.489
CsO	$r(\text{Cs}-\text{O})$	2.298	2.323	2.329	2.338
Cs ₂ O	$r(\text{Cs}-\text{O})$	2.368	2.382	2.382	2.390
	$\theta(\text{CsOCs})$	180.0	180.0	180.0	180.0
CsOH	$r(\text{Cs}-\text{O})$	2.373	2.392	2.409	2.416
	$r(\text{O}-\text{H})$	0.961	0.961	0.962	0.962
	$\theta(\text{CsOH})$	180.0	180.0	180.0	180.0
Cs ₂ (OH) ₂	$r(\text{Cs}-\text{O})$	2.674	2.690	2.698	2.702
	$r(\text{O}-\text{H})$	0.962	0.962	0.963	0.963
	$\theta(\text{CsOCs})$	98.3	97.7	97.1	97.0
	$\theta(\text{OCsO})$	81.7	82.3	82.9	83.0
	$\theta(\text{CsOH})$	130.8	131.1	131.3	131.5
	$\phi(\text{OCsOCs})$	0.0	0.0	0.0	0.0
	$\phi(\text{HOCsO})$	180.0	180.0	180.0	180.0
CsCl	$r(\text{Cs}-\text{Cl})$	2.903	2.910	2.920	2.925
Cs ₂ Cl ₂	$r(\text{Cs}-\text{Cl})$	3.127	3.132	3.138	3.140
	$\theta(\text{CsClCs})$	93.1	93.1	92.9	93.0
	$\theta(\text{ClCsCl})$	86.9	86.9	87.1	87.0
	$\phi(\text{ClCsClCs})$	0.0	0.0	0.0	0.0
CsBr	$r(\text{Cs}-\text{Br})$	3.072	3.075	3.084	3.087
Cs ₂ Br ₂	$r(\text{Cs}-\text{Br})$	3.285	3.289	3.294	3.296
	$\theta(\text{CsBrCs})$	91.0	90.9	91.0	91.0
	$\theta(\text{BrCsBr})$	89.0	89.1	89.0	89.0
	$\phi(\text{BrCsBrCs})$	0.0	0.0	0.0	0.0
CsI	$r(\text{Cs}-\text{I})$	3.304	3.271	3.320	3.303
Cs ₂ I ₂	$r(\text{Cs}-\text{I})$	3.511	3.502	3.522	3.511
	$\theta(\text{CsICs})$	88.0	83.5	88.0	87.6
	$\theta(\text{ICsI})$	92.0	96.5	92.0	92.4
	$\phi(\text{ICsICs})$	0.0	0.0	0.0	0.0

^a Bond lengths r are in angstroms, bond angles θ and bond dihedrals ϕ are in degrees.**Table 5**Scaled vibrational frequencies in cm⁻¹ calculated at different levels of theory.

Species	Level of theory			
	MP2/ECP46MDF		MP2/ECP46MWB	
Cs ₂	35		35	
	MP2/cc-pVTZ		MP2/aug-cc-pVTZ	
	ECP46MDF	ECP46MWB	ECP46MDF	ECP46MWB
CsH	883	885	874	877
CsO	361	351	341	340
Cs ₂ O	68, 68, 124, 456	68, 68, 124, 455	69, 69, 121, 450	68, 68, 121, 452
CsOH	336, 336, 385, 3702	335, 335, 378, 3702	349, 349, 361, 3704	350, 350, 360, 3705
Cs ₂ (OH) ₂	67, 69, 162, 231, 241, 248, 251, 263, 300, 302, 3695, 3695	66, 66, 166, 233, 239, 245, 285, 295, 318, 320, 3687, 3687	65, 65, 160, 227, 231, 239, 299, 307, 321, 324, 3688, 3688	65, 65, 163, 228, 233, 240, 299, 307, 325, 328, 3689, 3689
CsCl	209	209	204	204
Cs ₂ Cl ₂	41, 52, 132, 146, 150, 158	41, 51, 131, 146, 149, 158	41, 50, 129, 144, 148, 155	41, 51, 130, 145, 149, 156
CsBr	146	146	144	144
Cs ₂ Br ₂	28, 41, 95, 106, 108, 111	28, 41, 95, 106, 108, 110	28, 40, 93, 104, 106, 109	28, 41, 94, 105, 106, 109
CsI	118	124	115	118
Cs ₂ I ₂	21, 33, 78, 87, 89, 89	20, 26, 71, 84, 84, 91	22, 33, 78, 86, 87, 87	21, 32, 74, 82, 88, 89

differences (10–40%) by comparison to the other literature values than the other vibrational modes.

3.2. Standard enthalpies of formation at 298 K

The standard enthalpies of formation ($\Delta_f H_{298\text{K}}^\circ$) values for the 12 cesium-containing species were determined at all levels of theory

using both atomization and isogyric reactions. The latter reactions correspond to reactions in which the number of electron pairs in reactants and products is conserved. The standard enthalpies of formation at 298 K for each target species are derived from the calculated reaction enthalpies and evaluated (literature) enthalpies for the reference species in the work reactions. In the case of the atomization reaction, the standard enthalpies of formation at

298 K for the gaseous atoms (H, O, Cl, Br, I, and Cs) were taken from the NIST-JANAF thermochemical database [8] whose values are 217.999, 249.17, 121.302, 111.86, 106.76 and 76.5 kJ mol⁻¹, respectively. The set of isogyric reactions used in this work is the following



The standard enthalpies of formation at 298 K for the reference species [8] involved in the reactions (R1)–(R12) are 0, 38.987, –241.826, –92.312, –36.44, and 26.359 kJ mol⁻¹ for H₂, OH, H₂O, HCl, HBr, and HI, respectively. The ab initio vibrational frequencies for these species were multiplied by an appropriate scaling factor taken from the NIST-Computational Chemistry Comparison and Benchmark DataBase [49] (0.950 and 0.953 at the MP2/cc-pVTZ and MP2/aug-cc-pVTZ levels of theory, respectively).

Tables 6–11 gather the calculated $\Delta_f H_{298\text{K}}^\circ$ values using both atomization and isogyric reactions with the CCSD(T)/aug-cc-pVnZ (n = T, Q, 5), CBS/Halkier, and CBS/Peterson single-point energy calculations on both MP2/cc-pVTZ and MP2/aug-cc-pVTZ optimized geometries.

3.2.1. Influence of the geometry optimization level of theory

For each species, the $\Delta_f H_{298\text{K}}^\circ$ values are very consistent when using the same single-point energy level of theory on the different geometries (MP2/cc-pVTZ and MP2/aug-cc-pVTZ). As shown for example in Table 8, the computed $\Delta_f H_{298\text{K}}^\circ$ (Cs₂(OH)₂) using the ECP46MWB basis set for cesium and the isogyric reaction R6 are in kJ mol⁻¹ –647.9 and –647.1 at the CCSD(T)/aug-cc-pV5Z//MP2/cc-pVTZ and CCSD(T)/aug-cc-pV5Z//MP2/aug-cc-pVTZ levels of theory, respectively. The differences in the computed values for the same single-point energy level of theory are lower than 1 kJ mol⁻¹ with the exception of the cesium iodide dimer for which

the observed differences range from 1.2 to 1.7 kJ mol⁻¹ with the ECP46MWB basis set. These results show that the computed standard enthalpies of formation at 298 K do not depend on the geometry optimization level of theory when employing the MP2 method and the Dunning's correlation consistent basis sets (cc-pVTZ and aug-cc-pVTZ).

3.2.2. Influence of the cesium basis set

When increasing the cesium basis set size from ECP46MDF to ECP46MWB, the observed changes on the calculated standard enthalpies of formation at 298 K using either the atomization or the isogyric reactions are small to moderate. For each level of theory, the calculated differences between the ECP46MDF and ECP46MWB basis sets do not exceed 1 kJ mol⁻¹ for Cs₂, CsH, CsO, CsOH, Cs₂(OH)₂, CsCl, Cs₂Cl₂, and CsBr. The largest differences (up to 2.3 kJ mol⁻¹) are noticed for Cs₂O, Cs₂Br₂, CsI, and Cs₂I₂.

3.2.3. Influence of the basis sets for H, O, Cl, Br, and I atoms

The basis set in the CCSD(T) single-point energy calculation does affect significantly the $\Delta_f H_{298\text{K}}^\circ$ values. The noted effect on the standard enthalpy of formation at 298 K by the basis set size (aug-cc-pVQZ vs aug-cc-pVTZ) is in agreement with the strong anionic character of OH, Cl, Br, and I moieties in the affected compounds, the proper description of which requires augmented and large basis sets.

3.2.3.1. Atomization reactions. Increasing the basis sets size from aug-cc-pVTZ to aug-cc-pVQZ changes drastically the computed values by more than 8 kJ mol⁻¹ for all cesium-containing species with the exception of CsH. The highest differences (20–30 kJ mol⁻¹) have been observed for the dimers (Cs₂(OH)₂, Cs₂Cl₂, Cs₂Br₂, and Cs₂I₂). For example, the changes in the $\Delta_f H_{298\text{K}}^\circ$ (Cs₂I₂) values correspond to –27.0 kJ mol⁻¹ when going from the CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ to the CCSD(T)/aug-cc-pVQZ//MP2/cc-pVTZ whatever the cesium basis set. Less marked trends are observed when going from the aug-cc-pVQZ to the aug-cc-pV5Z basis sets with calculated differences ranging from about 8 to 10 kJ mol⁻¹ for the dimers.

3.2.3.2. Isogyric reactions. Adding more diffuse functions to the Dunning's basis sets tends also to decrease the computed standard enthalpies of formation 298 K. Increasing the basis sets size from aug-cc-pVTZ to aug-cc-pVQZ changes the values by less than –6 kJ mol⁻¹ for Cs₂, CsH, CsO, Cs₂O, CsOH, Cs₂(OH)₂, CsCl, CsBr, CsI, and Cs₂I₂. It can be noticed that the differences are slightly more important for Cs₂Cl₂ and Cs₂Br₂ than for the other cesium-

Table 6

Calculated standard enthalpies of formation at 298 K in kJ mol⁻¹ at different levels of theory using the atomization and isogyric reactions including spin–orbit corrections for Cs₂ and CsH.

SPC level of theory	Cs ₂				CsH			
	Atomization		Isogyric (R1)		Atomization		Isogyric (R2)	
	ECP46MDF	ECP46MWB	ECP46MDF	ECP46MWB	ECP46MDF	ECP46MWB	ECP46MDF	ECP46MWB
CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ	113.3	112.5	109.5	108.7	123.8	123.9	119.9	120.0
CCSD(T)/aug-cc-pVQZ//MP2/cc-pVTZ	113.3	112.5	112.1	111.2	121.2	121.1	119.9	119.8
CCSD(T)/aug-cc-pV5Z//MP2/cc-pVTZ	113.3	112.5	112.8	112.0	119.9	119.7	119.4	119.2
CBS/Halkier//MP2/cc-pVTZ	113.3	112.5	113.6	112.8	118.5	118.2	118.8	118.5
CBS/Peterson//MP2/cc-pVTZ	113.3	112.5	113.3	112.5	119.1	118.8	119.0	118.8
CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ	113.3	112.5	109.4	108.6	123.7	123.7	119.8	119.9
CCSD(T)/aug-cc-pVQZ//MP2/aug-cc-pVTZ	113.3	112.5	112.0	111.2	121.1	121.0	119.8	119.7
CCSD(T)/aug-cc-pV5Z//MP2/aug-cc-pVTZ	113.3	112.5	112.8	112.0	119.8	119.6	119.3	119.1
CBS/Halkier//MP2/aug-cc-pVTZ	113.3	112.5	113.6	112.8	118.4	118.1	118.7	118.4
CBS/Peterson//MP2/aug-cc-pVTZ	113.3	112.5	113.2	112.4	119.0	118.8	118.9	118.7
Experimental values (literature)		107.37 ± 0.30 [8] 109.4 ± 2.0 [10] 109.405 [12,13]				116.859 [12,13] 115.949 [14]		

The italicized values corresponds to literature (experimental) values.

Table 7
Calculated standard enthalpies of formation at 298 K in kJ mol^{-1} at different levels of theory using the atomization and isogyric reactions including spin–orbit corrections for CsO and Cs_2O .

SPC level of theory	CsO				Cs ₂ O			
	Atomization		Isogyric (R3)		Atomization		Isogyric (R4)	
	ECP46MDF	ECP46MWB	ECP46MDF	ECP46MWB	ECP46MDF	ECP46MWB	ECP46MDF	ECP46MWB
CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ	30.9	31.4	22.6	23.1	−117.7	−116.0	−135.3	−133.7
CCSD(T)/aug-cc-pVQZ//MP2/cc-pVTZ	22.4	23.0	20.6	21.2	−132.7	−130.8	−138.0	−136.1
CCSD(T)/aug-cc-pV5Z//MP2/cc-pVTZ	18.6	19.0	18.3	18.8	−139.4	−137.5	−141.7	−139.8
CBS/Halkier//MP2/cc-pVTZ	14.5	14.9	16.0	16.3	−146.3	−144.6	−145.5	−143.8
CBS/Peterson//MP2/cc-pVTZ	16.3	16.7	17.0	17.4	−143.2	−141.5	−143.8	−142.0
CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ	30.6	31.3	22.4	23.1	−117.7	−116.0	−134.9	−133.3
CCSD(T)/aug-cc-pVQZ//MP2/aug-cc-pVTZ	22.2	23.0	20.5	21.3	−132.6	−130.7	−137.6	−135.7
CCSD(T)/aug-cc-pV5Z//MP2/aug-cc-pVTZ	18.5	19.1	18.4	19.0	−139.2	−137.4	−141.2	−139.4
CBS/Halkier//MP2/aug-cc-pVTZ	14.6	15.0	16.1	16.5	−146.1	−144.3	−144.9	−143.2
CBS/Peterson//MP2/aug-cc-pVTZ	16.3	16.8	17.1	17.6	−143.0	−141.2	−143.3	−141.5
Experimental values (literature)		62.8 ± 41.8 [8] 38.2 ± 10.0 [10]				−92.0 ± 41.8 [8] −159 ± 25 [10] −142.862 [12,13]		

The italicized values corresponds to literature (experimental) values.

Table 8
Calculated standard enthalpies of formation at 298 K in kJ mol^{-1} at different levels of theory using the atomization and isogyric reactions including spin–orbit corrections for CsOH and $\text{Cs}_2(\text{OH})_2$.

SPC level of theory	CsOH				Cs ₂ (OH) ₂			
	Atomization		Isogyric (R5)		Atomization		Isogyric (R6)	
	ECP46MDF	ECP46MWB	ECP46MDF	ECP46MWB	ECP46MDF	ECP46MWB	ECP46MDF	ECP46MWB
CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ	−230.2	−230.5	−247.0	−247.3	−604.5	−605.5	−639.7	−640.7
CCSD(T)/aug-cc-pVQZ//MP2/cc-pVTZ	−244.6	−244.6	−249.0	−249.0	−632.7	−633.3	−643.3	−643.8
CCSD(T)/aug-cc-pV5Z//MP2/cc-pVTZ	−249.5	−249.6	−250.9	−251.1	−642.6	−643.4	−647.2	−647.9
CBS/Halkier//MP2/cc-pVTZ	−254.6	−254.9	−252.9	−253.3	−653.0	−653.9	−651.3	−652.3
CBS/Peterson//MP2/cc-pVTZ	−252.3	−252.6	−252.1	−252.3	−648.3	−649.2	−649.5	−650.4
CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ	−230.8	−230.7	−247.2	−247.1	−605.1	−605.7	−639.5	−640.3
CCSD(T)/aug-cc-pVQZ//MP2/aug-cc-pVTZ	−245.0	−244.6	−249.1	−248.8	−633.0	−633.3	−642.9	−643.2
CCSD(T)/aug-cc-pV5Z//MP2/aug-cc-pVTZ	−249.8	−249.6	−250.9	−250.8	−642.7	−643.1	−646.7	−647.1
CBS/Halkier//MP2/aug-cc-pVTZ	−254.8	−254.8	−252.8	−252.9	−652.9	−653.4	−650.7	−651.2
CBS/Peterson//MP2/aug-cc-pVTZ	−252.6	−252.5	−252.0	−251.9	−648.4	−648.8	−648.9	−649.4
Experimental values (literature)		−259.4 ± 12.6 [8] −257.0 ± 3.0 [10] −256.0 ± 5 [11] −252.7 ± 4.1 [19–20]				−687.8 ± 41.8 [8] −642.0 ± 5.0 [10] −653.0 ± 8 [11] −652.4 ± 11.7 [19–20]		

The italicized values corresponds to literature (experimental) values.

Table 9
Calculated standard enthalpies of formation at 298 K in kJ mol^{-1} at different levels of theory using the atomization and isogyric reactions including spin–orbit corrections for CsCl and Cs_2Cl_2 .

SPC level of theory	CsCl				Cs ₂ Cl ₂			
	Atomization		Isogyric (R7)		Atomization		Isogyric (R8)	
	ECP46MDF	ECP46MWB	ECP46MDF	ECP46MWB	ECP46MDF	ECP46MWB	ECP46MDF	ECP46MWB
CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ	−224.1	−224.3	−233.9	−234.2	−603.4	−604.3	−623.0	−624.0
CCSD(T)/aug-cc-pVQZ//MP2/cc-pVTZ	−235.4	−235.6	−239.2	−239.5	−627.6	−628.6	−635.5	−636.3
CCSD(T)/aug-cc-pV5Z//MP2/cc-pVTZ	−239.3	−239.6	−240.4	−240.7	−636.0	−636.8	−638.1	−638.9
CBS/Halkier//MP2/cc-pVTZ	−243.4	−243.8	−241.5	−242.0	−644.6	−645.4	−640.9	−641.7
CBS/Peterson//MP2/cc-pVTZ	−241.6	−242.0	−241.0	−241.4	−640.8	−641.6	−639.6	−640.4
CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ	−224.3	−224.6	−234.1	−234.4	−603.8	−604.4	−623.3	−624.0
CCSD(T)/aug-cc-pVQZ//MP2/aug-cc-pVTZ	−235.5	−235.7	−239.3	−239.6	−628.1	−628.6	−635.7	−636.3
CCSD(T)/aug-cc-pV5Z//MP2/aug-cc-pVTZ	−239.4	−239.7	−240.4	−240.7	−636.2	−636.8	−638.3	−638.9
CBS/Halkier//MP2/aug-cc-pVTZ	−243.5	−243.8	−241.6	−242.0	−644.7	−645.4	−641.0	−641.6
CBS/Peterson//MP2/aug-cc-pVTZ	−241.6	−242.0	−241.1	−241.4	−640.9	−641.5	−639.8	−640.4
Experimental values (literature)		−240.16 ± 4.2 [8] −240.162 [12,13]				−659.82 ± 10.5 [8] −659.817 [12,13] −644.658 [14]		

The italicized values corresponds to literature (experimental) values.

containing species (about 12 kJ mol^{-1}). As for the atomic reactions, less marked trends are observed when going from the aug-cc-pVQZ to the aug-cc-pV5Z basis sets.

3.2.4. Influence of the complete basis set extrapolation method

If the total energy is somewhat sensitive to the choice of the formula for the CBS estimation, the energy differences are not. As it

Table 10

Calculated standard enthalpies of formation at 298 K in kJ mol^{-1} at different levels of theory using the atomization and isogyric reactions including spin–orbit corrections for CsBr and Cs_2Br_2 .

SPC level of theory	CsBr				Cs ₂ Br ₂			
	Atomization		Isogyric (R9)		Atomization		Isogyric (R10)	
	ECP46MDF	ECP46MWB	ECP46MDF	ECP46MWB	ECP46MDF	ECP46MWB	ECP46MDF	ECP46MWB
CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ	−199.9	−200.7	−200.4	−201.3	−548.7	−550.5	−549.8	−551.6
CCSD(T)/aug-cc-pVQZ//MP2/cc-pVTZ	−210.7	−211.4	−205.2	−205.9	−573.3	−574.7	−562.3	−563.6
CCSD(T)/aug-cc-pV5Z//MP2/cc-pVTZ	−214.7	−215.3	−208.1	−208.7	−582.1	−583.3	−568.8	−570.0
CBS/Halkier//MP2/cc-pVTZ	−218.9	−219.4	−211.1	−211.6	−591.3	−592.3	−575.6	−576.7
CBS/Peterson//MP2/cc-pVTZ	−217.1	−217.6	−209.8	−210.3	−587.2	−588.3	−572.6	−573.7
CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ	−200.0	−200.8	−200.6	−201.4	−549.0	−550.9	−550.2	−552.1
CCSD(T)/aug-cc-pVQZ//MP2/aug-cc-pVTZ	−210.8	−211.5	−205.4	−206.0	−573.6	−575.0	−562.7	−564.1
CCSD(T)/aug-cc-pV5Z//MP2/aug-cc-pVTZ	−214.8	−215.4	−208.2	−208.8	−582.3	−583.6	−569.1	−570.4
CBS/Halkier//MP2/aug-cc-pVTZ	−219.0	−219.5	−211.2	−211.7	−591.4	−592.5	−575.9	−577.0
CBS/Peterson//MP2/aug-cc-pVTZ	−217.1	−217.6	−209.9	−210.4	−587.4	−588.5	−572.9	−574.1
Experimental values (literature)	−209.200 [12,13]				−565.829 [14]			

The italicized values corresponds to literature (experimental) values.

Table 11

Calculated standard enthalpies of formation at 298 K in kJ mol^{-1} at different levels of theory using the atomization and isogyric reactions including spin–orbit corrections for CsI and Cs_2I_2 .

SPC level of theory	CsI				Cs ₂ I ₂			
	Atomization		isogyric (R11)		Atomization		Isogyric (R12)	
	ECP46MDF	ECP46MWB	ECP46MDF	ECP46MWB	ECP46MDF	ECP46MWB	ECP46MDF	ECP46MWB
CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ	−154.9	−155.6	−154.9	−155.7	−450.5	−451.6	−450.6	−451.8
CCSD(T)/aug-cc-pVQZ//MP2/cc-pVTZ	−166.9	−167.8	−156.4	−157.3	−477.5	−478.7	−456.6	−457.7
CCSD(T)/aug-cc-pV5Z//MP2/cc-pVTZ	−170.8	−171.5	−156.0	−156.6	−486.6	−487.3	−456.8	−457.5
CBS/Halkier//MP2/cc-pVTZ	−175.0	−175.4	−155.5	−155.9	−496.1	−496.3	−457.1	−457.3
CBS/Peterson//MP2/cc-pVTZ	−173.2	−173.6	−155.7	−156.2	−491.9	−492.3	−457.0	−457.4
CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ	−155.0	−156.2	−155.2	−156.4	−450.9	−453.1	−451.3	−453.5
CCSD(T)/aug-cc-pVQZ//MP2/aug-cc-pVTZ	−167.0	−168.3	−156.6	−157.9	−477.8	−480.1	−457.0	−459.3
CCSD(T)/aug-cc-pV5Z//MP2/aug-cc-pVTZ	−170.9	−171.9	−156.0	−157.1	−486.8	−488.7	−457.1	−458.9
CBS/Halkier//MP2/aug-cc-pVTZ	−175.1	−175.8	−155.5	−156.2	−496.3	−497.6	−457.2	−458.5
CBS/Peterson//MP2/aug-cc-pVTZ	−173.2	−174.1	−155.7	−156.6	−492.1	−493.6	−457.1	−458.7
Experimental values (literature)	−154.3 ± 2.1 [10]				−464.3 ± 5.1 [10]			
	−154.960 [12,13]				−466.380 [12,13]			
	−152.32 ± 3 [15]				−470.56 ± 10 [20]			
	−153.27 ± 4.2 [20]							

The italicized values corresponds to literature (experimental) values.

can be seen in Tables 6–11, the CBS/Halkier values are close to the ones estimated by the mixed exponential/Gaussian function designed as CBS/Peterson in this work.

3.2.5. Comparison with the literature data

3.2.5.1. Cs₂, CsH. Firstly, it can be noticed in Table 6 that the CBS calculations (Halkier and Peterson) tend to slightly overestimate the $\Delta_f H_{298\text{K}}^\circ(\text{Cs}_2)$ and $\Delta_f H_{298\text{K}}^\circ(\text{CsH})$ values by comparison to the experimental values. A good agreement is however observed for the cesium dimer with the value from Cordfunke and Konings [10] if its uncertainty is taken into consideration.

3.2.5.2. CsO. The examination of the literature data given in Table 2 shows that there a lot of discrepancies between the values taken from the NIST-JANAF [8] database ($62.8 \pm 41.8 \text{ kJ mol}^{-1}$) and from the Cordfunke and Konings [10] ($38.2 \pm 10.0 \text{ kJ mol}^{-1}$). All our CBS estimates do not agree with the literature data even if the large uncertainties are given for the CsO radical.

3.2.5.3. Cs₂O. The literature data are scattered with values ranging in kJ mol^{-1} from (-92.0 ± 41.8) [8] to (-159 ± 25) [10]. As shown in Table 7, all our CBS standard enthalpies of formation at 298 K are in excellent agreement with the $-142.862 \text{ kJ mol}^{-1}$ taken from the Thermodata database [12,13].

Table 12

Average^a standard enthalpies of formation at 298 K in kJ mol^{-1} .

Species	$\Delta_f H_{298\text{K}}^\circ$ – this work
Cs ₂	112.6
CsH	118.6
CsO	17.0
Cs ₂ O	−142.6
CsOH	−252.6
Cs ₂ (OH) ₂	−650.8
CsCl	−241.7
Cs ₂ Cl ₂	−641.0
CsBr	−211.0
Cs ₂ Br ₂	−575.4
CsI	−156.2
Cs ₂ I ₂	−458.0

^a Mean values calculated at the CBS/Halkier + ECP46MWB//MP2/cc-pVTZ + ECP46MWB, CBS/Peterson + ECP46MWB//MP2/cc-pVTZ + ECP46MWB, CBS/Halkier + ECP46MWB//MP2/aug-cc-pVTZ + ECP46MWB, and CBS/Peterson + ECP46MWB//MP2/aug-cc-pVTZ + ECP46MWB levels of theory.

3.2.5.4. CsOH, Cs₂(OH)₂, CsCl, and Cs₂Cl₂. As reported in Tables 8 and 9, the calculated $\Delta_f H_{298\text{K}}^\circ$ are in excellent agreement with their literature counterparts if the experimental uncertainties are taken into consideration.

3.2.5.5. CsBr, Cs₂Br₂, CsI, and Cs₂I₂. The examination of the literature data shows that there are few available data for CsBr and Cs₂Br₂. It can be noticed that there are large differences between the computed CBS standard enthalpies of formation at 298 K using either the atomization or the isogyric reaction. As seen in Tables 10 and 11, the calculated differences are about 7, 14, 17, 35 kJ mol^{−1} for CsBr, Cs₂Br₂, CsI, and Cs₂I₂, respectively. By comparison to the numerous experimental values for CsI and Cs₂I₂, the best estimates are obtained using the isogyric reactions. The calculated

$\Delta_f H_{298K}^\circ(\text{CsBr})$ is therefore in excellent agreement with the $-209.200 \text{ kJ mol}^{-1}$ value taken from the Thermodata database [12,13]. In the case of the cesium bromide dimer, the standard enthalpy of formation at 298 K differ by about 10–15 kJ mol^{−1} from the value given in the SGTE database [14].

3.2.6. Average $\Delta_f H_{298K}^\circ$ values for the Cs-containing species

The $\Delta_f H_{298K}^\circ$ values calculated with both CBS calculation methods (Halkier and Peterson) can be considered as the measurements

Table 13

Calculated standard molar entropies at 298 K (S_{298K}°) and heat capacities at constant pressure ($C_p(T)$) in J K^{−1} mol^{−1} from optimized geometries, scaled vibrational frequencies, and moments of inertia at different levels of theory for Cs₂, CsH, CsO, Cs₂O, CsOH, and Cs₂(OH)₂.

Species	Level of theory	S_{298K}°	$C_{p,300}$	$C_{p,400}$	$C_{p,500}$	$C_{p,600}$	$C_{p,800}$	$C_{p,1000}$	$C_{p,1500}$
Cs ₂ $\sigma^a = 2$	MP2/ECP46MDF	285.947	37.395	37.404	37.408	37.410	37.413	37.414	37.415
	MP2/ECP46MWB	285.815	37.395	37.404	37.408	37.410	37.412	37.413	37.414
CsH $\sigma = 1$	MP2/cc-pVTZ + ECP46MDF	214.902	31.320	32.909	34.081	34.895	35.866	36.380	36.935
	MP2/cc-pVTZ + ECP46MWB	214.926	31.311	32.900	34.073	34.888	35.861	36.377	36.933
	MP2/aug-cc-pVTZ + ECP46MDF	214.987	31.380	32.973	34.136	34.941	35.897	36.402	36.945
	MP2/aug-cc-pVTZ + ECP46MWB	215.007	31.361	32.953	34.119	34.926	35.887	36.395	36.942
	MP2/cc-pVTZ + ECP46MWB								
CsO $\sigma = 1$	MP2/cc-pVTZ + ECP46MDF	248.754	35.865	36.496	36.812	36.991	37.113	37.259	37.346
	MP2/cc-pVTZ + ECP46MWB	247.255	35.693	36.391	36.741	36.940	37.144	37.240	37.337
	MP2/aug-cc-pVTZ + ECP46MDF	247.485	35.781	36.443	36.777	36.965	37.159	37.250	37.341
	MP2/aug-cc-pVTZ + ECP46MWB	247.574	35.790	36.450	36.781	36.968	37.160	37.251	37.342
	MP2/cc-pVTZ + ECP46MWB								
Cs ₂ O $\sigma = 2$	MP2/cc-pVTZ + ECP46MDF	314.657	59.324	60.504	61.123	61.481	61.854	62.032	62.212
	MP2/cc-pVTZ + ECP46MWB	314.927	59.356	60.525	61.137	61.491	61.860	62.036	62.214
	MP2/aug-cc-pVTZ + ECP46MDF	314.728	59.366	60.532	61.142	61.495	61.862	62.038	62.215
	MP2/aug-cc-pVTZ + ECP46MWB	315.127	59.369	60.533	61.143	61.496	61.862	62.038	62.215
	MP2/cc-pVTZ + ECP46MWB								
CsOH $\sigma = 1$	MP2/cc-pVTZ + ECP46MDF	252.595	48.869	50.957	52.032	52.701	53.699	54.674	56.997
	MP2/cc-pVTZ + ECP46MWB	252.853	48.936	51.000	52.062	52.722	53.712	54.683	57.001
	MP2/aug-cc-pVTZ + ECP46MDF	252.741	48.858	50.953	52.030	52.700	53.698	54.672	56.994
	MP2/aug-cc-pVTZ + ECP46MWB	252.755	48.847	50.946	52.026	52.696	53.695	54.670	56.993
	MP2/cc-pVTZ + ECP46MWB								

Table 14

Calculated standard molar entropies at 298 K (S_{298K}°) and heat capacities at constant pressure ($C_p(T)$) in J K^{−1} mol^{−1} from optimized geometries, scaled vibrational frequencies, and moments of inertia at different levels of theory for CsCl, Cs₂Cl₂, CsBr, Cs₂Br₂, CsI, and Cs₂I₂.

Species	Level of theory	S_{298K}°	$C_{p,300}$	$C_{p,400}$	$C_{p,500}$	$C_{p,600}$	$C_{p,800}$	$C_{p,1000}$	$C_{p,1500}$
CsCl $\sigma^a = 1$	MP2/cc-pVTZ + ECP46MDF	255.934	36.752	37.034	37.169	37.243	37.318	37.353	37.387
	MP2/cc-pVTZ + ECP46MWB	255.980	36.754	37.035	37.170	37.244	37.318	37.353	37.388
	MP2/aug-cc-pVTZ + ECP46MDF	256.224	36.784	37.053	37.181	37.252	37.323	37.356	37.389
	MP2/aug-cc-pVTZ + ECP46MWB	256.236	36.781	37.051	37.180	37.251	37.322	37.356	37.389
Cs ₂ Cl ₂ $\sigma = 4$	MP2/cc-pVTZ + ECP46MDF	390.738	81.731	82.341	82.628	82.785	82.942	83.015	83.087
	MP2/cc-pVTZ + ECP46MWB	391.018	81.747	82.350	82.634	82.789	82.944	83.017	83.088
	MP2/aug-cc-pVTZ + ECP46MDF	391.568	81.781	82.370	82.647	82.798	82.949	83.020	83.089
	MP2/aug-cc-pVTZ + ECP46MWB	391.348	81.767	82.362	82.642	82.795	82.947	83.018	83.089
CsBr $\sigma = 1$	MP2/cc-pVTZ + ECP46MDF	267.395	37.082	37.226	37.293	37.330	37.367	37.385	37.402
	MP2/cc-pVTZ + ECP46MWB	267.412	37.082	37.226	37.293	37.330	37.367	37.385	37.402
	MP2/aug-cc-pVTZ + ECP46MDF	267.610	37.094	37.233	37.298	37.334	37.369	37.386	37.402
	MP2/aug-cc-pVTZ + ECP46MWB	267.607	37.093	37.232	37.297	37.333	37.369	37.386	37.402
Cs ₂ Br ₂ $\sigma = 4$	MP2/cc-pVTZ + ECP46MDF	414.991	82.410	82.729	82.878	82.960	83.041	83.078	83.115
	MP2/cc-pVTZ + ECP46MWB	415.180	82.418	82.734	82.881	82.962	83.042	83.079	83.116
	MP2/aug-cc-pVTZ + ECP46MDF	415.551	82.434	82.743	82.887	82.966	83.044	83.080	83.116
	MP2/aug-cc-pVTZ + ECP46MWB	415.590	82.431	82.741	82.886	82.965	83.044	83.080	83.116
CsI $\sigma = 1$	MP2/cc-pVTZ + ECP46MDF	275.145	37.198	37.292	37.336	37.360	37.384	37.395	37.406
	MP2/cc-pVTZ + ECP46MWB	274.520	37.172	37.277	37.327	37.354	37.381	37.393	37.405
	MP2/aug-cc-pVTZ + ECP46MDF	275.402	37.207	37.297	37.339	37.363	37.386	37.396	37.407
	MP2/aug-cc-pVTZ + ECP46MWB	275.116	37.196	37.291	37.336	37.360	37.384	37.395	37.406
Cs ₂ I ₂ $\sigma = 4$	MP2/cc-pVTZ + ECP46MDF	432.886	82.656	82.869	82.968	83.022	83.076	83.101	83.125
	MP2/cc-pVTZ + ECP46MWB	436.341	82.695	82.891	82.982	83.032	83.081	83.104	83.127
	MP2/aug-cc-pVTZ + ECP46MDF	432.817	82.664	82.874	82.971	83.024	83.077	83.101	83.126
	MP2/aug-cc-pVTZ + ECP46MWB	434.049	82.680	82.883	82.977	83.028	83.079	83.103	83.126

^a Symmetry number.

of the same quantity, the true enthalpy of formation. The calculated arithmetic averages of the $\Delta_f H_{298K}^\circ$ based on four different calculation methods (CBS/Halkier//MP2/cc-pVTZ, CBS/Peterson//MP2/cc-pVTZ, CBS/Halkier//MP2/aug-cc-pVTZ, and CBS/Peterson//MP2/aug-cc-pVTZ) using the isogyric reaction and the most extended basis set for cesium (ECP46MWB) are gathered in Table 12. The calculated $\Delta_f H_{298K}^\circ$ values are in excellent agreement with most recent experimental values with the exception of CsO and Cs₂Br₂.

3.3. Standard molar entropies and heat capacities at constant pressure

From the molecular properties obtained at the MP2/cc-pVTZ and MP2/aug-cc-pVTZ levels of theory with the two different basis sets for cesium (ECP46MDF and ECP46MWB), the standard molar entropies (S_{298K}°) and heat capacities at constant pressure ($C_p(T)$, $300 \leq T/K \leq 1500$) were calculated using the rigid rotor harmonic oscillator approximation with the Thermo.pl program [56]. Their values are listed in Tables 13 and 14. Available literature values are also listed in Table 2. There is an excellent agreement between our calculated S_{298K}° and the corresponding literature values for the 12 studied species. The values taken from the NIST-JANAF [8] database for CsO and Cs₂(OH)₂ are not in agreement with our results as well as the other literature values. The calculated heat capacities at constant pressure are generally in excellent agreement at 300 K with their literature counterparts. The largest differences between our calculations and the literature values are observed for Cs₂O (about 7%).

4. Conclusion

High level CCSD(T)/CBS with spin-orbit corrections have been made to assess the thermochemical properties ($\Delta_f H_{298K}^\circ$, S_{298K}° , $C_p = f(T)$) of 12 cesium-containing species of nuclear safety interest (Cs₂, CsH, CsO, Cs₂O, CsOH, Cs₂(OH)₂, CsCl, Cs₂Cl₂, CsBr, Cs₂Br₂, CsI, and Cs₂I₂). The standard enthalpies of formation at 298 K were calculated using both atomization and isogyric reactions at the CCSD(T)/aug-cc-pVnZ//MP2/cc-pVTZ ($n = T, Q, 5$), CBS/Halkier//MP2/cc-pVTZ, CBS/Peterson//MP2/cc-pVTZ, CCSD(T)/aug-cc-pVnZ//MP2/aug-cc-pVTZ ($n = T, Q, 5$), CBS/Halkier//MP2/aug-cc-pVTZ, and CBS/Peterson//MP2/aug-cc-pVTZ levels of theory. Two basis sets (ECP46MDF and ECP46MWB) were employed for the cesium atom. Standard molar entropies at 298 K and heat capacities at constant pressure were estimated at the MP2/cc-pVTZ and MP2/aug-cc-pVTZ levels of theory. Based on our theoretical results, the use of both CBS extrapolation methods (Halkier or Peterson) combined with the isogyric reaction is a valuable solution to obtain accurate standard enthalpies of formation at 298 K for cesium-containing species within chemical accuracy of experimental values with the exception of the CsO and Cs₂Br₂ species. Based on the excellent agreement observed between our calculated $\Delta_f H_{298K}^\circ$ values and their literature counterparts, the standard enthalpies of formation at 298 K are estimated to be the following: $\Delta_f H_{298K}^\circ$ (CsO) = 17.0 kJ mol⁻¹ and $\Delta_f H_{298K}^\circ$ (Cs₂Br₂) = -575.4 kJ mol⁻¹. The use of MP2 method allows also computing precisely the standard molar entropies at 298 K and the temperature dependence of the heat capacities.

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