



Matrix-isolation FT-IR study of $(\text{CsBr})_n$ and $(\text{CsI})_n$ ($n = 1-3$)

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ABSTRACT

The species present in the vapours of CsBr and CsI have been isolated in krypton and xenon matrices and were investigated by FT-IR spectroscopy in the range of 180–30 cm⁻¹. The recorded spectra revealed the presence of substantial amounts of dimer beside the alkali halide monomers. The assignment of the bands and characterization of the fundamentals was carried out on the basis of DFT quantum chemical calculations. The applied B3P86 exchange-correlation functional in conjunction with the Stuttgart-Cologne relativistic effective core potentials and polarized triple-zeta valence basis set reproduced the accurate experimental monomer Cs–Br and Cs–I bond distances within 0.001 Å, and the harmonic stretching frequency within 1.1 cm⁻¹. Based on calculations at this level we report reliable geometrical parameters and fundamental frequencies for the dimer and trimer species $(\text{CsBr})_n$ and $(\text{CsI})_n$. Utilizing the computed data we propose the identification of the E' asymmetric stretching mode of the trimer $(\text{CsI})_3$ trapped in a Xe matrix and that of $(\text{CsBr})_3$ in Kr and Xe matrices.

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1. Introduction

Caesium bromide and iodide are potential components of high-pressure metal halide discharge lamp fillings. Knowledge of the physico-chemical properties of these compounds, in particular on their interaction with several lanthanide halide salts, is of great importance to the development of these efficient light sources [1]. CsI is of particular interest also in nuclear technology being one of the main fission products. Due to its high volatility, it can appear in the high-temperature (gas-phase) transport processes within nuclear reactors as well as in the environment at accidental situations [2–8]. The essential properties to model the processes involving these compounds are the enthalpy of formation of the gaseous species and their thermodynamic functions, usually derived by statistical thermodynamics from their molecular geometry and vibrational frequencies.

The vapourization behaviour of both CsBr and CsI has been studied (see e.g. Refs. [9–11] and references cited therein). For both systems, the monomer was observed as the main vapour species, while the vapour also contained a substantial amount of

dimers and a very small amount (less by ca. three orders of magnitude) of trimers [10,12]. The next oligomer, the tetramer appears in the vapour phase by another order of magnitude below the trimer [10,13]. Hilpert et al. reported dissociation enthalpies for $(\text{CsBr})_2$ [10] and $(\text{CsI})_3$ [13]. These data and additional dissociation enthalpies evaluated by us on the basis of heat of formations from Refs. [14,15] are compiled in the [Supplementary Materials](#) together with the dissociation enthalpies obtained from the present quantum chemical calculations.

Regarding the geometry, accurate experimental data are available on the Cs–Br and Cs–I bond distances in the monomers from microwave spectroscopic measurements [16] as well as on CsI from its vibration-rotation spectrum [17]. The molecular parameters of the dimer and trimer species are less well known. The low molar ratios of $(\text{CsBr})_2$ and $(\text{CsI})_2$ molecules (around 5%) found in the gas electron diffraction measurements by Hartley and Fink [18,19] did not facilitate an evaluation of their geometrical parameters with proper accuracy.

Today's sophisticated quantum chemical methods can supplement missing experimental molecular data. The highest-level ab initio calculations reported recently on the ground- and excited-states properties of CsI by Kurosaki et al. were performed at the MRSDCI+Q level using extended basis set for both Cs and I [20]. Prior theoretical studies include semi-empirical ionic model approaches up to the alkali halide tetramers [21,22] as well as standard quantum chemical calculations (HF, MP2, B3LYP in conjunction with relativistic effective core potentials and double-zeta valence basic set) on the monomers and dimers [23,24]. Since the

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semi-empirical models fitted the parameters to the experimental data of the monomers, the ionic model studies provided better results than the standard quantum chemical calculations, where the bond distances of CsBr and CsI were reproduced by deviations of 0.1 Å or even worse. This obviously limits the reliability of the dimer data computed at these levels of theory. We did not find any quantum chemical calculation on the trimers of the title halides in the literature. For the evaluation of their thermodynamic properties [13] the mentioned ionic model results [21] were used.

Previous IR spectroscopic measurements of the target caesium halides include the study of matrix-isolated CsI and CsBr in solid Ar [25] and a gas-phase FT-IR measurement of CsI [26]. In both studies absorption bands could be assigned to the dimer species as well. In addition, detailed vibrational information on the stretching fundamental of the monomers has been obtained from the MW spectra by Honerjäger and Tischer [27] extended for CsI on the basis of the vibration-rotation spectrum from infrared emission spectroscopy [17].

Our motivation with the present study was to provide accurate and unambiguous structural and vibrational data on the dimers and trimers of the title caesium halides. We performed FT-IR experiments on the vapour species trapped in krypton and xenon matrices. The experiments have been performed under various conditions, varying from strongly diluted to highly concentrated matrices. The formation of oligomers was promoted by making deposits as heavy as possible. In order to assist the assignment and provide reliable geometrical data, we performed DFT quantum chemical calculations. To achieve the best possible theoretical model of these systems, we performed numerous test calculations with various exchange-correlation functionals and extended basis sets. In the present paper we include only the results obtained at the best level of theory judged by comparison with the bond distances of the monomers [16].

2. Methods

2.1. Vibrational spectroscopic experiments

The samples of solid CsBr and CsI used for the experiments were provided by NRG, Petten, The Netherlands (99.9%). The samples were used without further purification as X-ray diffraction analysis showed the samples to be phase pure.

The apparatus for the matrix-isolation experiments consisted of a Displex DE 202 cryotip (Air Products and Chemicals, Allentown, PA), which can be rotated in a home-made stainless steel vacuum shroud. The temperature of the deposition window was between 18–25 and 20–23 K during formation of the Xe and Kr matrices, respectively. The detailed description of the matrix-isolation equipment is given in Ref. [28]. The CsBr evaporations were performed in the temperature range 930–955 K, deposition times varied between 30 and 90 min. The temperature range of the CsI evaporations was 875–925 K, also with deposition times between 30 and 90 min. High purity xenon 4.5 or krypton 4.5 was employed as the isolating gas without further purification. The matrix gas was generally deposited at a rate of 0.5–0.8 ml/min. Contact of the moisture- and oxygen-sensitive samples with ambient atmosphere during filling of the equipment could be avoided by using the glass-cartridge method from Klotzbücher et al. [29] adapted for high-temperature evaporation conditions. The samples were contained in narrow graphite tubes, which in turn were surrounded by a quartz tube, sealed under high vacuum conditions. Prior to the filling of the cells in an argon-filled glove box, both the graphite inner tube and the quartz tube were outgassed for 12 h under 5% H₂/95% Ar atmosphere. After reaching a vacuum of 10⁻⁵ mbar in the matrix-

Table 1
Geometrical parameters of (CsBr)_n and (CsI)_n (n = 1–3).

Molecule	Method	Cs–X (Å)	X–Cs–X (°)	Cs–X–Cs (°)
CsBr	MW ^b	3.07221 (5)		
	ED ^c	3.065 (4)		
	B3P86 ^a	3.073		
(CsBr) ₂	ED ^c	3.356 (28)	85.0 (1.8)	
	B3P86 ^a	3.310	90.2	89.8
(CsBr) ₃	B3P86 ^a	3.318	119.7	120.3
CsI	MW ^b	3.31515 (6)		
	ED ^d	3.314 (6)		
	IR ^e	3.31519042 (40)		
	IR ^f	3.3150949 (177)		
	MRSDCI+Q ^g	3.3327		
	B3P86 ^a	3.315		
(CsI) ₂	ED ^d	3.572 (166)	96.5 (8.2)	
	B3P86 ^a	3.553	93.4	86.6
(CsI) ₃	B3P86 ^a	3.560	123.9	116.1

^a This work. The computed data have been obtained using the B3P86 exchange-correlation density functional [31,32] in conjunction with small-core relativistic effective core potentials [33–35].

^b Equilibrium bond distances determined by microwave spectroscopy [16].

^c Bond distances derived from gas electron diffraction experiments [18]. For the monomer the equilibrium bond distance has been evaluated, while for the dimer the distance is given as an *r*_a parameter.

^d Bond distances derived from gas electron diffraction experiments [19]. For the monomer the equilibrium bond distance has been evaluated, while for the distance in the dimer *r*_a parameter is given.

^e Equilibrium bond distances determined from the vibration-rotation spectrum of CsI using the Dunham potential [17].

^f Equilibrium bond distances determined from the vibration-rotation spectrum of CsI using the Born-Oppenheimer potential [17].

^g Computed at the MRSDCI+Q level using extended basis set for both Cs and I [20].

isolation equipment, the top of the quartz tube was opened by a hammer mounted on the heat shield.

The IR spectra of matrix-isolated species in the 180–30 cm⁻¹ range were recorded in reflection mode with a Bomem DA3.02 Fourier-transform spectrometer equipped with a Bomem APG 7400D mirror bench. A home-made vacuum flange connected the cryostat to the interferometer. For detection a helium-cooled germanium bolometer operating at 4.2 K was used. Measurements were performed through a wedged polyethylene window in the vacuum shroud. Resolution was 0.5 cm⁻¹ or better; 256 scans were co-added. The spectra were baseline corrected and the water rotation bands resulting from residual molecules in the evacuated spectrometer were subtracted.

2.2. Computational details

On the basis of test calculations on CsBr and CsI using various exchange-correlation functionals in conjunction with the relativistic effective core potentials (RECP) of the Stuttgart-Cologne group [30] and various valence basis sets we chose the B3P86 [31,32] DFT method. To obtain the final data published here we used for Cs the RECP with 46 electrons in the core and a valence basis set of triple-zeta quality extended by polarization (3f2g) and diffuse functions [33]. For Br and I RECPs with 10 and 28 electrons in the core, respectively, were applied in conjunction with valence basis sets of cc-pVTZ quality [34,35]. All the computations were carried out with the Gaussian 03 program [36].

3. Results and discussion

The computed geometrical parameters for CsBr, CsI, (CsBr)₂, (CsI)₂, (CsBr)₃ and (CsI)₃ are compiled in Table 1. The excellent agreement between the computed and the accurate experimental equilibrium bond distances of the monomers [16] supports the reliability of our selected computational level. The agreement

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