



Ionic species in vapour over barium diiodide: Quantum chemical study of structure and thermodynamic properties



Fortunatus Jacob^{a,b,*}, Tatiana P. Pogrebnyaya^a, Alexander M. Pogrebnoi^a

^a Department of Materials, Energy Science and Engineering, The Nelson Mandela African Institution of Science and Technology (NM-AIST), P.O. Box 447, Nelson Mandela Rd, Tengeru, Arusha, Tanzania

^b Department of Chemistry, University of Dar es Salaam, Tanzania

ARTICLE INFO

Article history:

Received 1 July 2017

Accepted 20 August 2017

Available online 22 August 2017

Keywords:

Cluster ions

Geometrical structure

Vibrational spectra

Barium diiodide

Enthalpies of formation

Thermodynamic functions

DFT

MP2 and MP4

ABSTRACT

The cluster ions $Ba_2I_3^+$, $Ba_3I_5^+$ and $Ba_4I_7^+$ were detected earlier in saturated vapour over barium diiodide using high temperature mass spectrometric technique. In this work the structure and thermodynamic properties of the species BaI_3^- , $Ba_2I_3^+$, $Ba_3I_5^+$, $Ba_4I_7^+$, and $Ba_5I_9^+$ have been studied theoretically by using the density functional theory (DFT/B3P86) and Møller–Plesset perturbation theory (MP2 and MP4) with triple-zeta valence basis sets. The enthalpies of ion molecular reactions have been determined both theoretically and based on available experimental data; the enthalpies of formation of the cluster ions are found as follows (in kJ mol^{-1}): -709 ± 6 , (BaI_3^-), -96 ± 10 ($Ba_2I_3^+$), -654 ± 15 ($Ba_3I_5^+$), -1177 ± 20 ($Ba_4I_7^+$) and -1686 ± 20 ($Ba_5I_9^+$).

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Structure of alkaline earth metal halides has been the captivating subject for many researchers and therefore this group of halides is extensively studied [1–9]; most efforts were focused on the neutral molecular species [1,10–14]. Much fewer investigations were devoted to the ionic vapour composition. Different cluster ions were revealed in equilibrium vapours over alkaline earth dihalides using high temperature mass spectrometric technique: $M_2X_3^+$, $M_3X_5^+$, $M_4X_7^+$ [4,5] ($M = \text{Ca, Sr, Ba}$; $X = \text{F, Cl, Br}$ or I), and $BaCl_3^-$ [6]. Moreover the ions $SrCl^+$, $Sr_2Cl_3^+$, and $SrCl_3^-$ and BaF^+ , $Ba_2F_3^+$, BaF_3^- were detected as formed through thermal emission from the crystalline $SrCl_2$ and BaF_2 at elevated temperatures under conditions of free-surface and Knudsen cell evaporation [7,8]. Gas-phase alkaline earth halide anions, MgX_3^- , CaX_3^- ($X = \text{Cl, Br}$), were produced using electrospray and investigated by photoelectron spectroscopy [9].

Research in this field is driven by the numerous applications of the cluster ions owing to their unique optical, electronic and

magnetic properties [15–17]. Cluster ions may be considered as potential building blocks of new materials [15,17,18] and good candidates in assembling crystals [16]. Also they are useful in chemical vapour transport and deposition [19–21], for application in magnetohydrodynamic generators [22], ion implantation technologies [23], ion thrusters [24], and also in aerospace investigations [25,26]. These high-tech applications drive a need for more understanding of properties of cluster ions.

The structure and properties of the CaCl -, BaCl -, BaF - and BaBr -cluster ions were studied theoretically earlier [27–30]. This work focuses on the BaI -containing ions, negative BaI_3^- and positive $\text{BaI}^+(\text{BaI}_2)_n$ ($n = 1-4$). The properties to be considered are the geometrical structures, vibrational spectra, enthalpies of dissociation reactions and enthalpies of formation of the ionic species. Furthermore, based on the geometrical parameters and vibrational frequencies obtained the thermodynamic functions of the species are to be computed and applied for the treatment of previously measured equilibrium constants of ion molecular reactions [4,5] so as to obtain thermodynamic properties which are named below as ‘based on experiment’ values.

2. Computational details

Two methods were employed to compute the geometrical parameters and vibrational spectra of the species: (i) electron

* Corresponding author at: Department of Materials, Energy Science and Engineering, The Nelson Mandela African Institution of Science and Technology (NM-AIST), P.O. Box 447, Nelson Mandela Rd, Tengeru, Arusha, Tanzania.

E-mail addresses: fortunatusjacob@yahoo.com (F. Jacob), tatiana.pogrebnyaya@nm-aist.ac.tz, pgamtp@mail.ru (T.P. Pogrebnyaya), alexander.pogrebnoi@nm-aist.ac.tz (A.M. Pogrebnoi).

density function theory (DFT) with the Becke–Perdew functional (B3P86) [31–33] and (ii) Møller–Plesset perturbation theory of the second order (MP2). The computations were performed using the Firefly QC package [34] which is partially based on the GAMESS (US) [35] source code. The basis sets used were the def2-tzvp 6s4p3d1f with quasirelativistic effective core potential (ECP) for the barium atom [11] and SDB-aug-cc-pvtz 4s4p3d2f with relativistic ECP for iodine atom [36]; the basis sets with ECPs were accessed from the EMSL library (The Environmental Molecular Sciences laboratory, US) [37]. For calculations where the MP2 method was employed, no orbitals were frozen, the script N CORE = 0 was used. The geometrical structures of the species were visualized using ChemCraft [38] and MacMolPlt [39] software. The vibrational spectra were computed and analysis was done to assign the frequencies to certain normal modes and confirm the geometrical structures to be equilibrium.

The enthalpies of dissociation reactions $\Delta_r H^\circ(0)$ and enthalpies of formation $\Delta_f H^\circ(0)$ of the cluster ions have been determined applying two approaches, ‘pure theoretical’ and ‘based on experiment’, as described earlier [27,28]. The DFT, MP2 and MP4 methods were used to calculate theoretical enthalpies of dissociation reactions of the species. In addition the correction for the basis set superposition error (BSSE) [40] with counterpoise (CP) method [41] was taken into account for the MP2 and MP4 results. The details of this procedure can be found in [28]. For the DFT method, the BSSE with CP correction was not implemented because it had been shown to be not much sensitive to this correction in previous studies [42,43]. For the second approach, the thermodynamic functions (TD) of the ions considered have been calculated within the ‘rigid rotator-harmonic oscillator’ approximation; the OpenThermo software [44] was used. The required TD functions and enthalpies of formation of the $I_{(g)}$, $BaI_{2(g)}$ and $BaI_{2(c)}$ were retrieved from the Ivtanthermo database [45]. For the BaI^+ , the enthalpy of formation $\Delta_f H^\circ(BaI^+, g, 0 K) = 490.2 \text{ kJ mol}^{-1}$ was found through the ionization energy of BaI [46] ($IE(BaI) = 5.08 \text{ eV}$) and the enthalpy of formation of gaseous BaI [45] ($\Delta_f H^\circ(BaI, g, 0 K) = -7.126 \text{ kJ mol}^{-1}$).

3. Results and discussion

3.1. Geometrical structure and vibrational spectra of the species

3.1.1. Simple species BaI, BaI^+ and BaI_2

The geometrical parameters, vibrational frequencies, ionization energies, total energies and dipole moments were calculated for the simple species BaI, BaI^+ and BaI_2 using the DFT and MP2 methods. The results are compared with the available reference data as presented in Table 1. One can see for all three species the calculated internuclear separations $R_e(\text{Ba–I})$ are shorter for DFT method as compared to MP2, by 0.046 Å, 0.022 Å and 0.026 Å for BaI, BaI^+ and BaI_2 , respectively. For the valence angle $\alpha_e(\text{I–Ba–I})$ of the BaI_2 molecule, the value by DFT is larger by 7.5° than that by MP2 method. Similar trend for the calculated geometrical parameters in general was observed for other similar barium halide species, the increase from DFT to MP2 being about 0.01–0.02 Å for the $R_e(\text{–Ba–X})$ values and 2°–10° for the angle as shown in the previous studies [27–29].

There are no reliable reference data for internuclear separation $R_e(\text{Ba–I})$ of the species BaI and BaI^+ . For the BaI_2 , the experimental geometrical parameters obtained by electron diffraction method are available in [50]; our calculated parameters both by DFT and MP2 methods do not contradict the experimental data. The computed vibrational frequencies of the species BaI and BaI_2 are generally in a good agreement with available literature data, both theoretical [1,3] and experimental [47,50].

Table 1
Properties of BaI, BaI^+ and BaI_2 .

Property	DFT	MP2	Reference
BaI			
$R_e(\text{Ba–I})$	3.111	3.157	
$-E$	37.06614	36.71099	
ω_e	148	146	152.3 ^a ; 150.05 ^b
$q(\text{Ba})$	0.663		
$-q(\text{I})$	0.663		
IE_{ad}	5.18	5.00	5.08 ± 0.04 ^c
IE_v	5.24	5.07	
μ_e	6.0		
BaI^+			
$R_e(\text{Ba–I})$	2.987	3.009	
$-E$	36.87578	36.52737	
ω_e	185	183	
$q(\text{Ba})$	1.526	1.619	
$-q(\text{I})$	0.526	0.619	
BaI_2			
$R_e(\text{Ba–I})$	3.140	3.166	3.150 ± 0.007 ^d
$\alpha_e(\text{I–Ba–I})$	134.2	141.7	148.0 ± 0.9 ^d
$-E$	48.64184	48.17090	
$\omega_1(A_1)$	129	125	106 ± 12 ^d
$\omega_2(A_1)$	22	18	~16 ^d
$\omega_3(B_1)$	164	167	145 ± 21 ^d
$q(\text{Ba})$	1.467	1.574	
$-q(\text{I})$	0.734	0.787	
IE_{ad}	8.62		8.6 ^e
IE_v	8.88	9.2	8.74 ± 0.01 ^f
μ_e	6.6	6.0	

Here and hereafter $R_e(\text{Ba–I})$ is the equilibrium internuclear distance, Å; $\alpha_e(\text{I–Ba–I})$ is the valence angle, degrees; ω_i are the vibrational frequencies, cm^{-1} ; IE_{ad} and IE_v are the adiabatic and vertical ionization energies, respectively, eV; and μ_e is the dipole moment, D.

^a Emission spectra in flames [47].

^b Laser excitation spectra [48] retrieved from NIST [49].

^c Evaluation [46], retrieved from NIST [49].

^d Electron diffraction [50].

^e Appearance energy [51].

^f Photoelectron spectroscopy [52].

The Mulliken atomic charges shown in Table 1 indicate an ionic nature of the species. As is seen the excessive negative charge on the iodine atoms rises in the series $BaI^+ \text{–} BaI \text{–} BaI_2$: 0.526e – 0.663e – 0.734e that indicates an increase in ionicity of Ba–I bonds.

We have analyzed the frontier MOs of the species (Fig. 1). One can see that for BaI^+ and BaI_2 the HOMOs are composed of *p*-AOs of the iodine atom(s) which are perpendicular to the bond(s) Ba–I; they look like non-bonding orbitals. The LUMO orbitals of the BaI^+ ion and BaI_2 molecule are composed mostly of the Ba *s*-AOs. When an electron attaches the BaI^+ ion resulting in BaI neutral molecule, this unpaired electron occupies the Ba *s*-AO (Fig. 1b and c). When one more iodine atom is added to BaI to form the BaI_2 molecule, the electron density redistribution occurs, doubly occupied HOMO being built from *p_z*-AOs of the I-atoms (Fig. 1d). Apparently the shape and orientation of the frontier orbitals illustrate the polar nature of bonds in the simple species considered.

Following the procedure from our previous studies [28,29], the ionization energies, adiabatic IE_{ad} and vertical IE_{ver} , were calculated. As for comparison with the experimental data, the computed IE_{ad} by MP2 method for BaI agrees better with that from [46] than the DFT result. For the BaI_2 , the IE_{ad} obtained by DFT method is in a very good accordance with the experimental data by photoelectron spectroscopy [52], the difference is as small as 0.02 eV. As for the IE_v of BaI_2 a fair agreement with the experimental data [52] is observed for the DFT result with the difference ~0.14 eV, while for the MP2 the discrepancy is high, 0.46 eV.

At the end of this section we can conclude that the calculations performed for the simple species validate the appropriateness of

Download English Version:

<https://daneshyari.com/en/article/5392270>

Download Persian Version:

<https://daneshyari.com/article/5392270>

[Daneshyari.com](https://daneshyari.com)