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Structure and thermodynamic properties of positive and negative cluster ions in saturated vapour over barium dichloride

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Structure and thermodynamic properties of positive and negative cluster ions in saturated vapour over barium dichloride

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Abstract

Geometrical structure, vibration spectra, and enthalpies of dissociation have been investigated for the ions BaCl3−, Ba2Cl3+, Ba3Cl5+, and Ba4Cl7+ which were detected earlier in the saturated vapour over BaCl2. Quantum chemical methods of density functional theory, the second and the fourth order Møller–Plesset perturbation theory have been applied. The effective core potential with cc-pVTZ basis set for barium atom and two full-electron basis sets including the diffuse and polarised basis functions for chlorine atom were used. The effect of the basis set size and the computation method on the results was analysed. According to the results, all the ions possess the compact shaped structure. The equilibrium geometrical structures were found as follows: the planar D3h for BaCl3−, triple bridged bipyramidal D3h for Ba2Cl3+, hexabridged D3h for Ba3Cl5+, and septuple bridged C2v for Ba4Cl7+. For positive ions, the different isomeric structures were considered, but no isomers for these ions have been found. The geometrical parameters and vibration frequencies were utilised for computing of thermodynamic functions of the ions, and then the thermodynamic functions were used for the treatment of the experimental mass spectrometric data. The enthalpies of formation ΔfH°(0 K) of the ions were determined (in kJ/mol): −994 ± 6 (BaCl3−), −481 ± 10 (Ba2Cl3+), −1276 ± 14 (Ba3Cl5+), −2048 ± 35 (Ba4Cl7+).

Keywords: barium chloride, positive and negative cluster ions, quantum mechanical calculations, geometrical structure, frequencies of vibrations, enthalpy of dissociation, enthalpy of formation