

Structure, temperature effect and bonding order analysis of hydrated bromide clusters



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ARTICLE INFO

Article history:

Received 29 April 2016

In final form 25 September 2016

Available online 7 October 2016

Keywords:

Hydrated halide

Bond order

Temperature effect

Basin-hopping

ABSTRACT

Halide ions have been received intense interest in charactering and understanding their implications in atmospheric chemistry since they are related to the ozone destruction in the stratosphere. In the current study, structures, thermodynamic properties, and spectroscopic signatures of hydrated bromide $\text{Br}^-(\text{H}_2\text{O})_n$ ($n = 1-8$) clusters are thoroughly studied and compared with available studies, the new global minima were observed for the larger size $\text{Br}^-(\text{H}_2\text{O})_{7,8}$ clusters. The numbers of isomer increase with the increasing water molecules, considering the growing complexity, the isomer populations of each size clusters are provided under a wide temperature range, it was shown that different type of structures possess different temperature dependences. In addition, the bond order of different bond types of hydrated bromide has been systematically investigated for the first time.

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1. Introduction

Halide-water cluster plays an important role in cluster science because of their unique spectroscopic and thermodynamic properties. In addition, they are also related to the catalytic reactions of ozone destruction in the atmosphere. These characteristics render them a useful simplified model to study the macro phenomenon, from the point of view of size, geometry, charge density, and spectroscopic details on chemical dynamics [1,2].

The structure and reactivity of water molecules with singly charged halide ions have been extensively investigated by both experiment and theory. Experimentally, size-selected halide ion-water complexes were first studied using high pressure mass spectrometry [3,4] and photoelectron spectroscopy [5,6]. More recently, infrared [7–9] and ZEKE [10,11] spectroscopies have been applied to probe the structures and kinetics of anionic halide-water clusters and their corresponding neutral counterparts. In particular, the Johnson group conducted extensive experimental work on a halide ion-water clusters via vibrational spectra and pro-

vided abundant spectroscopic data that yielded critical structural information [1,7,12–21].

Computer simulations can help to provide essential insight into the structures and dynamics of solvation shells around ions since the experimental determination is generally difficult. The abundance of experimental data on $\text{X}^-(\text{H}_2\text{O})_n$, ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{and I}$) clusters [1,7,12–21], motivated the theoreticians to use different methods, ranging from the empirically constructed potential energy surfaces [22–24] to quantum chemistry calculations [25–37], to explain the experimental findings.

In general, the potential energy surface of the hydrated molecular clusters supports a large number of minima, and the task of finding the lowest one is difficult and tedious. The minima are obtained through manual search in many studies. However, this method is less reliable for the large molecular systems with multiple local minima, which has motivated researchers to use various global optimization techniques to seek the local minima.

Neogi et al. evaluated the structures of halide-water clusters by stochastic search-based genetic algorithm in conjunction with density functional theory (GA-DFT) method [25]. Head-Gordon and coworkers [28] studied the effect of charge transfer of $\text{Cl-H}_2\text{O}$ dimers using the absolutely localized molecular orbital (ALMO) model. Jahangiri et al. described the interatomic interactions of halide hydration via self-consistent charge density

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functional tight binding (DFTB) method [33]. Kim et al. adopted time-dependent density-functional theory (TDDFT) to obtain the absorption maxima of $\text{Br}^-(\text{H}_2\text{O})_n$ clusters for the transitions from the ground states to the first excited states [29,31,32]. Recently, Jiang utilized the Basin-Hopping algorithm together with DFT (BH-DFT) to study the structures and energetics of $\text{Br}^-(\text{H}_2\text{O})_n$ clusters [26,27]. All of these methods are effective for investigating the halide hydrated clusters and these works indeed provide a comprehensive probe for the micro solvation of halide ion. However, the detailed bonding order investigations are rarely reported

since the interactions present in the clusters are coupling effects, which may lead to many interesting properties.

In the current work, modified BH-DFT method (a new compressed sampling skill was introduced [42]) has been employed to study the properties of hydrated bromide clusters and extent to the larger size, additionally, for the first time, temperature effect of different isomers with same size are studied at a relatively wide temperature range (50–450 K), the bond order of both the hydrogen bonds and hydrogen-halogen interactions of hydrated bromide clusters are also determined.

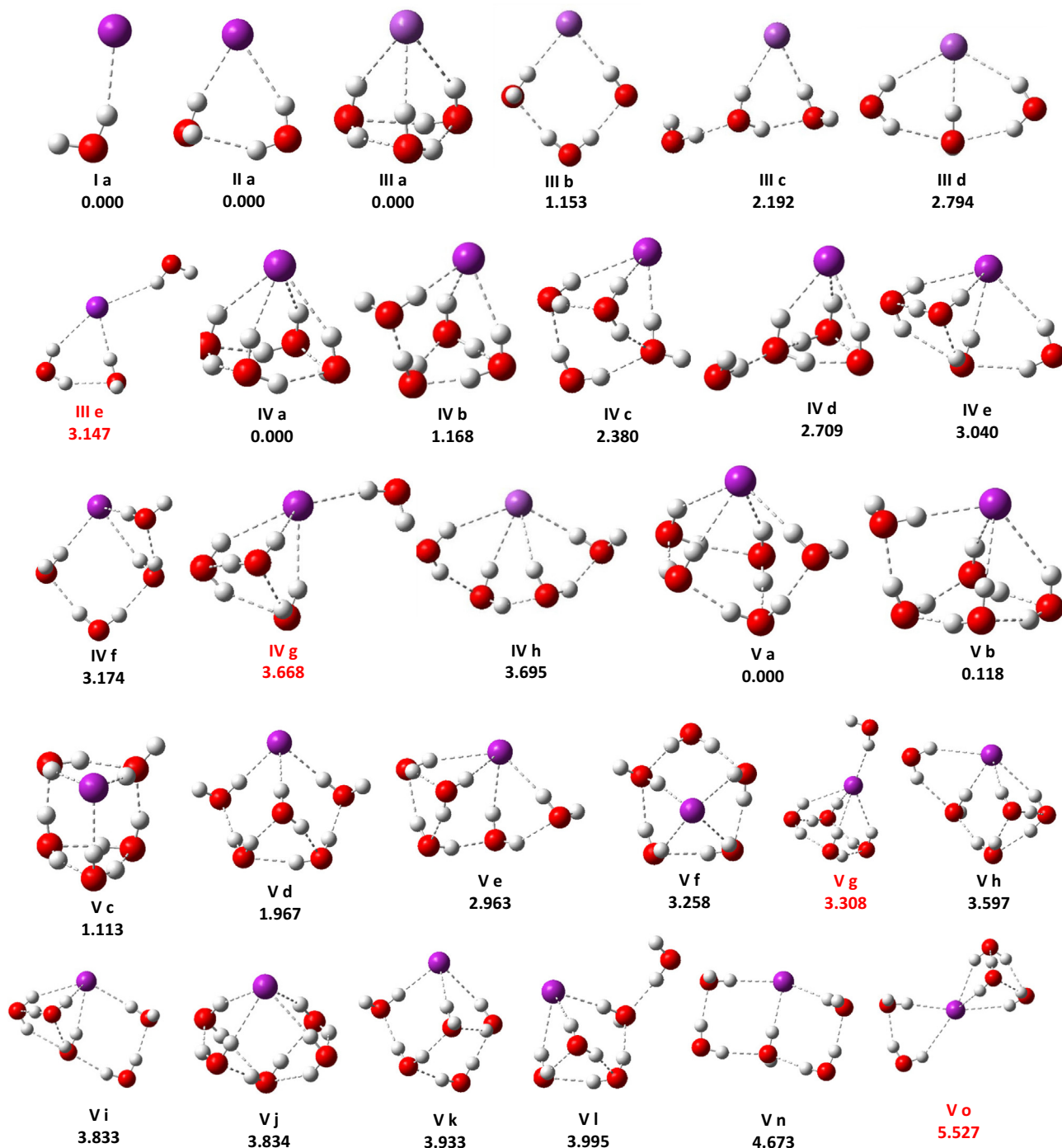


Fig. 1. Optimized low-lying geometries of $\text{Br}^-(\text{H}_2\text{O})_n$ ($n = 1-5$) at the B3LYP/aug-cc-pVTZ level of theory, ordered by increasing relative electronic energy (in kcal mol⁻¹) to the minimum energy isomer at 0 K and 1 atm. I, II, ... V represent $n = 1, 2, \dots, 5$. Red text indicates the structures of the interior type geometry. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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