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THEORETICAL AND EXPERIMENTAL EVALUATION OF K_2Br^+ AND K_3Br^+ CLUSTERS' IONIZATION ENERGIES

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ABSTRACT

In current study, a non-stoichiometric bromine-doped potassium K_2Br^+ and K_3Br^+ clusters are generated by combining a Knudsen effusion cell as a chemical reactor with thermal or surface ionization, and selected by a magnetic sector mass spectrometer. Furthermore, their ionization energies (IEs) are calculated for the first time using B3LYP/9-ve PP(K),cc-pVTZ-PP(Br) level of theory. Herein, presented results indicate that experimentally obtained IEs by Ionov equation, 4.10 ± 0.20 eV for K_2Br^+, and 4.03 ± 0.20 eV for K_3Br^+, are in consistence with their theoretically determined IEs.

INTRODUCTION

In the past decades, clusters, groups of constituents (atoms, molecules) connected with bounds of different strength, become increasingly attractive research field given that their formation and properties enable to investigate the gradual development of matter from the atom to the bulk. A clusters consisting of an alkali metal combined with more electronegative element exhibit unique physical and chemical phenomena, which are of both fundamental and technological significance. The very small bromine-doped potassium clusters violate stoichiometry based on the octet rule is the reason why such systems are called hyperpotassium or, more generally, hypervalent clusters.

Experimentally, K_2Br^+ cluster was detected the in vapor of KBr salt, using the Knudsen effusion method in the temperature range from 700 K to 890 K [1]. Further, this cluster was produced by electrospray ionization (ESI) [2]. The ionization energy (IE) of K_2Br^+ cluster was determined in our

previous experiments using a triple thermal or surface ionization source, confirming that this cluster belongs to the "superalkali" species, since its IE of 3.95 ± 0.1 eV is lower than the IE of K^+ [3].

Given that there is lack of experimental and theoretical evidence for existence of K_3Br^+ cluster while K_2Br^+ was obtained by different source of ionization, current study was undertaken to theoretically and experimentally evaluate IE of these clusters using Ionov equation and different source of ionization, respectively.

EXPERIMENTAL

The experimental method has been previously described [4]. Briefly, the rhenium (Re) filament was placed in the centre of the Knudsen effusion cell's base. The sample, KBr salt, was pressed as a ring and placed on the inner wall of the Knudsen effusion cell. The ions emitted from the surface of Re filament were extracted to a mass analyzer, a 12-inch radius, 90° magnetic sector. To determine IE of the clusters produced, the ion currents of K_nBr^+ (n = 2, 3) clusters were measured using K^+ ion for calibration as a function of the Re filament temperature. Furthermore, the IE of the clusters were calculated by the Ionov equation:

$\ln (I(K^+)/I(cluster^+))= (IE(cluster^+)-IE(K^+))/kT$.

Using 4.34 eV as the IE of K^+, and the values of the slopes of the plots $\ln (I(K^+)/I(cluster^+))= 1/T$ by this equation, the IE of clusters were obtained.

Theoretical calculations for the IE of K_2Br^+ and K_3Br^+ clusters were done on the CCSD(T)/9-ve PP(K),cc-pVTZ-PP(Br)//B3LYP/9-ve PP(K),cc-pVTZ-PP(Br) level of theory.

RESULTS AND DISCUSSION

In this work K_2Br^+ and K_3Br^+ clusters were detected the in vapor of KBr salt, using the Knudsen effusion method in the temperature range from 1150 to 1350 ˚K. The mass spectrum of the ionic beam K_nBr (n=2 and 3) is presented in Figure 1.

In order to determined of the IE the natural logarithm of the ion intensities for K_nBr^+ (n = 2, 3) are plotted in Figure 2 as a function of the inverse of Re filament temperature (1/T).

The ground electronic state structures of the lowest isomers of the neutral and charged K_nBr (n = 2, 3) clusters calculated at the B3LYP/9-ve PP(K),cc-pVTZ-PP(Br) level of theory is presented in Figure 2 [5], [6].

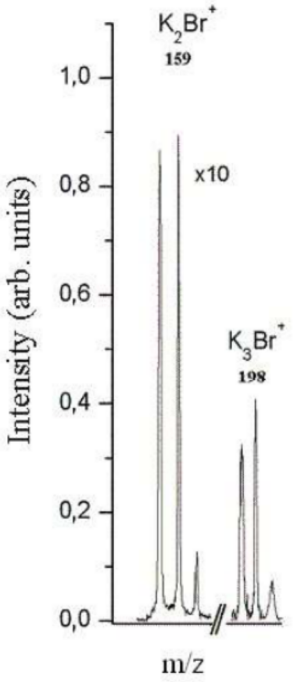

Figure 1. The mass spectrum of K_nBr^+ (n = 2, 3) cluster ions.

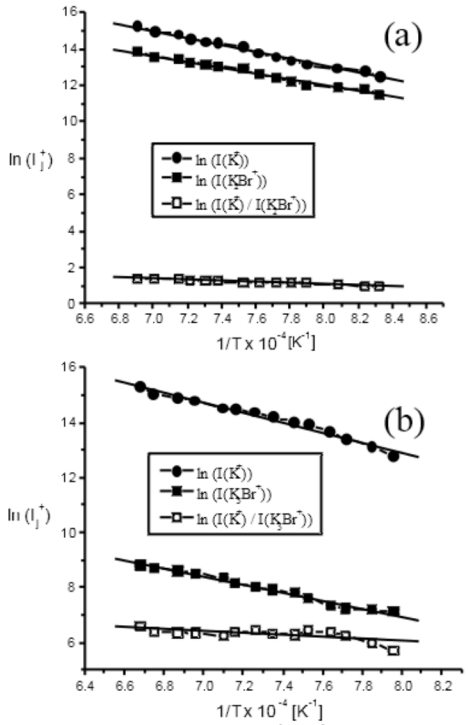

Figure 2. Plots of ln I_i^+ (I_i^+ - ion current of clusters) versus 1/T for (**a**) K_2Br^+ and (**b**) K_3Br^+ clusters.

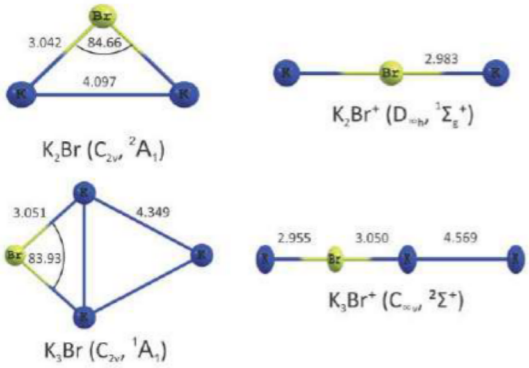

Figure 3. The ground electronic state structures of the lowest isomers of the neutral and charged K_nBr (n = 2, 3) clusters calculated at the B3LYP/9-ve PP(K),cc-pVTZ-PP(Br) level of theory. Bond lengths are in Å, angles in degrees.

As presented in Table 1, the experimentally obtained IE of K_nBr^+ and calculated IEs are in agreement within experimental uncertainties.

Table 1. Experimentally obtained and a*b initio* calculated adiabatic (aIE) and vertical (vIE) ionization energies (in eV) of neutral K_2Br^+ and K_3Br^+ in the $^2A_1$ and $^1A_1$ ground electronic states, respectively.

Species	aIE	vIE	Exp.
K_2Br^+ (C_{2v}, $^2A_1$)	3.31	3.96	4.10 ± 0.20
K_3Br^+ (C_{2v}, $^1A_1$)	3.76	4.28	4.03 ± 0.20

Since the IE of investigated clusters are lower than the IE of the potassium atom, the experimental setup presented in this paper provides a convenient way for generate "superalkali" clusters of the type K_nBr^+.

CONCLUSION

Being in accordance with theoretically obtained data for K_2Br^+ and K_3Br^+ clusters IE, the obtained experimental results showed that modified Knudsen effusion cell, a chemical reactor combined with thermal or surface ionization, is a suitable method for generation of investigated clusters.

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