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# Ionization energies of $K_2X$ (X=F, Cl, Br, I) clusters

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The electronic structure and properties of dipotassiummonohalides are important for understanding the unique physical and chemical behavior of $M_nX$ systems. In the present study, $K_2X$ (here X=F, Cl, Br, I) clusters were generated in the vapor over salts of the corresponding potassium halide, using a magnetic sector thermal ionization mass spectrometer. The ionization energies obtained for $K_2F$, $K_2Cl$, $K_2Br$, and $K_2I$ molecules were $3.82 \pm 0.1\,eV$, $3.68 \pm 0.1\,eV$, $3.95 \pm 0.1\,eV$, and $3.92 \pm 0.1$, respectively. These experimental values of ionization energies for $K_2X$ (X=F, Br, and I) are presented for the first time. The ionization energy of $K_2Cl$ determined by thermal ionization corresponds to previous results obtained by photoionization mass spectrometry, and it agrees with the theoretical ionization energy calculated by the *ab initio* method. The presently obtained results support previous theoretical predictions that the excess electron in dipotassiummonohalide clusters is delocalized over two potassium atoms, which is characteristic for F-center clusters. Copyright © 2011 John Wiley & Sons, Ltd.

A cluster is a small piece of material containing from three to several hundred atoms. Small clusters show properties which are very different from those of the bulk material, because of their small size.[1]

Alkali halide clusters of the type $M_nX_p$ (M is an alkali metal and X is a halogen) have given rise in the last decade to a number of experimental and theoretical papers. Particularly interesting is that changing the stoichiometry of the clusters of the type $M_nX_p$ (n versus p) may lead to a transition from insulator to metal (i.e. starting from a neutral stoichiometric ionic clusters with n=p such as $M_nX_n$, and successively substituting anions (X) by electrons, ultimately leads to a neutral metallic cluster $M_n$).[2–13]

Dipotassium monohalides belong to the class of alkali-excess systems of the type $M_nX$. Investigations of $M_nX$ clusters that contain single or multiple excess alkali atoms open a new dimension for studies of excess-electron localization and bonding in clusters.[14–16]

Only a few theoretical results are available for $K_2X$ (X=F, Cl, Br, I) clusters.[17–21] Schreyer has used the term 'hypervalent' for type $M_nX$ clusters and the term 'hyperpotassium' for $K_2X$ clusters (or molecules). The extra valence electrons in the hypervalent clusters are not associated with the halogen atom, but contribute to the formation of the metallic cage. The overall features can be described in terms of a negatively charged $X^-$, embedded in a positively charged metallic cage ($M_n^+$). As with other hypervalent molecules, the ionization energies of dipotassium monohalides are remarkably lower than that of the potassium atom.[20] In this respect, Gustev and Boldirev have called this cluster a 'superalkali'.[21–23]

The latest theoretical calculations have shown that these 'superalkalis' are of great importance in chemistry since they can mimic the characteristics of alkali metals and maintain their structural and electronic integrities when assembled with other species. Therefore, they can be used for the synthesis of compounds ('superatom') which contains a 'superalkali' and 'superhalogen' moiety. Li *et al*. predicted that superalkalis may serve as potential building blocks for the assembly of novel nanostructural materials with special properties.[24,25]

An ionization energy (IE) of $3.60\,eV$ for $K_2Cl$ was calculated by Ochsenfeld and Ahlrichs, while an experimental value of $3.50 \pm 0.1\,eV$ was measured by photoionization mass spectrometry.[19,26] To date, there are neither theoretical calculations nor experimental results for the IE of $K_2X$ (X=F, Br I).

Honea *et al*. have provided another approach to explain the chemical bonding of $M_nX$ type clusters. Their theoretical calculation showed that the excess electrons in alkali halides can be localized in an anion defect location, the so-called F center, for which ionization energies are around 4eV, at an alkali atom (the 'non-cubic' clusters; ionization energies around 5eV) or delocalized as a state in the conduction band (IE <2eV).[27,28] According to this classification, $K_2X$ species are F-center type clusters.

Hebant and Picard have investigated the relative stability of $M_2X$ (M=Li, Na, K, Rb, and X=F, Cl, Br, I) by means of Density Functional Theory (DFT) calculations combined with thermodynamic calculations. They called these clusters subhalides which play an important role at the liquid metal-molten salt interface.[29] Their study showed that all $K_2X$ clusters have $C_{2v}$ symmetry, and that the K–X bond lengths increase from fluorine to iodine, but the K-X-K angles decrease. They observed that the energy of formation increases from fluorine to iodine for $K_2X$ clusters (the DFT conditions: one molecule in vacuum, zero Kelvin and no pressure). As the alkali metal atomic number increases by substituting elements from Li to Cs, the corresponding subhalide is less stable.[29–33]

Experimental investigations have so far confirmed the existence of polymeric species ($K_nX_n$), non-stoichiometric ($K_nX_{n-1}$) and alkali excess clusters such as $K_nX$ (X-nonmetal).[34–42]

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These species were identified using mass spectrometry on their formation in vapors of the potassium halide salt. For example, Butman *et al*. investigated the kinetics of potassium chloride single crystal sublimation by magnetic sector mass spectrometry. They found that $K^+$, $KCl^+$, and $K_2Cl^+$ ions were formed via electron ionization fragmentation of KCl and $K_2Cl_2$ molecules in the temperature range 780–900K. The heated surface of a KCl crystal emits directly both positive ($K^+$, $K_2^+$, $K_2Cl^+$, $K_3Cl_2^+$) and negative ($Cl^-$, $Cl_2^-$, $KCl_2^-$) ions in the temperature ranges 710–1020K and 950–1020K, respectively. The currents of negative ions were much weaker than those of positive ions.[37,41] In addition, Butman *et al*. found that a potassium bromide single crystal, when heated above 700K, emits positive ions: $K^+$, $K_2^+$, $K_2Br^+$, and $K_3Br_2^+$.[38,39] Rykov *et al*. detected the $K_2F^+$ cluster in the vapor of a KF-$BeF_2$ salts mixture, using the Knudsen effusion method.[43]

Emission of the $K_2Cl^+$ ion was observed by electrospray ionization mass spectrometry (ESI-MS). Wang and Cole reported that in the homologous alkali halide series the relative abundances of $M_2X^+$ (M is an alkali metal and X is a halogen) ions increased with increasing size of either the cation (positive ion mode) or the anion (negative ion mode).[44]

The dipotassium chloride cluster has been formed using thermal ionization mass spectrometry (TIMS). Xiao *et al*. demonstrated that the intensity of $K_2Cl^+$ ions emitted by KCl is greatly enhanced by loading graphite onto the filament at a low temperature (below 300°C). However, to date, there are no experimental results for the ionization energies of the dipotassium chloride clusters obtained using TIMS.[45]

The goal of the present work is the study of conditions for the measurement of ionization energies of small heterogeneous $K_2X$ (X=F, Cl, Br, I) clusters by TIMS, and comparing these results with those for similar clusters of dilithium monohalides,[46–48] which we have studied previously. In addition, the influence of a halogen atom on the IE of small $K_2$ clusters was observed. We also investigated the influence of the different electron affinities of halogens (X=F, Cl, Br, I) on the ionization energies of $K_2X$.

## EXPERIMENTAL

Thermal ionization mass spectrometry is a method for generating ions at a hot metal surface (filament). In this study we used the triple filament thermal ionization technique and the ion source is shown in Fig. 1. The ion source is made of three rhenium filaments of the same dimension ($8\,mm \times 1\,mm$ $0.05\,mm$).

The mass analyzer was a 12-inch radius, 90° magnetic sector instrument of local design. The pressure in the analyzer region was maintained below $10^{-8}$ Torr, while the operating pressure in the source region was below $5 \times 10^{-7}$ Torr.

$K_2X^+$ ions were formed during heating of the appropriate salts of potassium halide KX (X=F, Cl, Br, I). Each of the dipotassium monohalide clusters was obtained in a separate measurement. The sample salts KX (X=F, Cl, Br, I) dissolved in $H_2O$ were deposited on the side filaments and then dried under a heat lamp. The advantage of the triple filament technique for thermal ionization is the possibility of heating the side filaments and the central filament separately.

In this experiment, the side filaments were used to evaporate the sample while the central filament was used for ionization of the neutral species. The mass spectrum of each cluster was obtained in a series of measurements (Fig. 2). The temperatures of the side filaments were 1317K for $K_2F$, 1040K for $K_2Cl$, 1079K for $K_2Br$ and 978K for $K_2I$, and the temperatures of the central filament were 1374K for $K_2F$, 1638K for $K_2Cl$, 1693K for $K_2Br$ and 1620K for $K_2I$. The filaments were heated using an electric current, and the temperature was determined by an optical pyrometer.

To calculate the ionization energies of the clusters produced, we used the method of comparison. The reference ion used in this work was the $K^+$ ion. The ion currents of $K_2X^+$ and $K^+$ were measured as a function of the temperature of the ionization filament. By calculating the logarithm of the ratio of the $K^+$ to $K_2X^+$ ion intensities at a series of temperatures, the difference in ionization energies of the two species may be obtained using the Saha-Langmuir equation:

$$I_i^+ = A\exp[(\Phi - IE_i)/kT]$$

where $I^+$ is the ion current ($i$ are $K^+$ and $K_2X^+$), A is the term containing the reflection coefficients and statistical weighting factors (constant with temperature), $\Phi$ is the work function of the ionization filament, IE is the ionization energy of the atoms or molecules, k is Boltzman's constant, and T is the temperature of the Re central filament. The actual value of $\Phi$ is strongly affected by the species adsorbed on the ionization filament and this uncertainty was avoided by simultaneous measurement of the ion intensities of the species of known ionization energy, K (4.34eV), and of the investigated clusters.
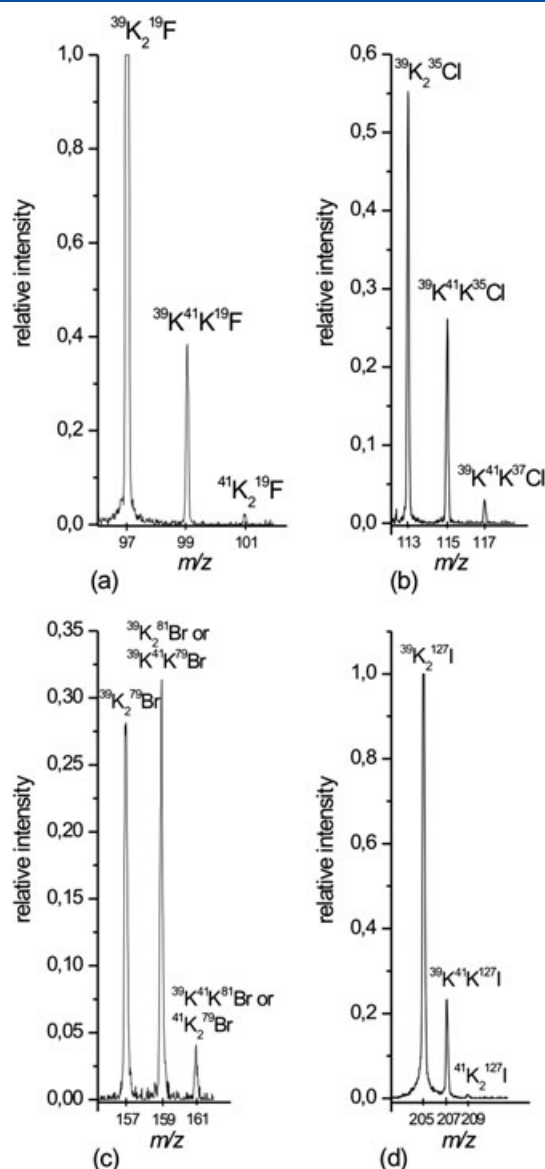
## RESULTS AND DISCUSSION

Identification of dipotassium monohalide clusters formed in the ion source was achieved from their *m/z* values, isotopic abundance, and ionization energy. The mass spectra of clusters $K_2X^+$ (X=F, Cl, Br, I) obtained by thermal ionization are presented in Fig. 2.

The assignment of the species was based on the pattern coefficients derived from the natural isotopic abundance of potassium (100% of $^{39}K$ and 7.2% of $^{41}K$) and of the corresponding halogen element (100% of $^{19}F$, 100% of $^{35}Cl$, 32.4% of $^{37}Cl$, 100% of $^{79}Br$, 97.5% of $^{81}Br$ and 100% of $^{127}I$). For example, the signals for the $K_2Cl$ cluster appeared at *m/z* 113, 115, 117. The observed pattern coefficients of 1, 0.468
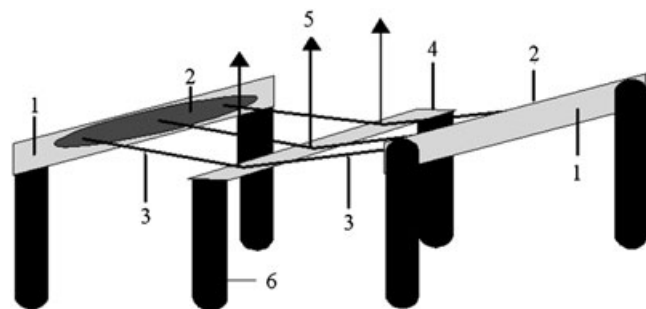


**Figure 1.** Ion source: 1, side filaments of Re; 2, potassium halide dissolved in water (sample); 3, evaporating sample; 4, central filament of Re; 5, ion beam of the $K_2X^+$ cluster; 6, filament holder.

**Figure 2.** Thermal ionization mass spectra of (a) dipotassium fluoride cluster, (b) dipotassium chloride cluster, (c) dipotassium bromide cluster, and (d) dipotassium iodide cluster.

the presumed candidates for species which might contribute to the $K_2X^+$ signal through dissociative ionization. However, evaporation of the $K_2X_2$ species is favored at temperatures below 900 K, while under our experimental conditions the temperature is much higher. In addition, if the dissociation ionization was dominant, the measured energy of the $K_2X$ ions would actually be the appearance energy of $K_2X$ from $K_2X_2$, which would be a much greater value than those given in Table 1. Therefore, we conclude that the processes of creating ions from dissociative ionization of dimers are not expected in this case. It was experimentally observed that an intensity increase in the $K^+$ ion produces an increase in the intensity of $K_2X^+$.
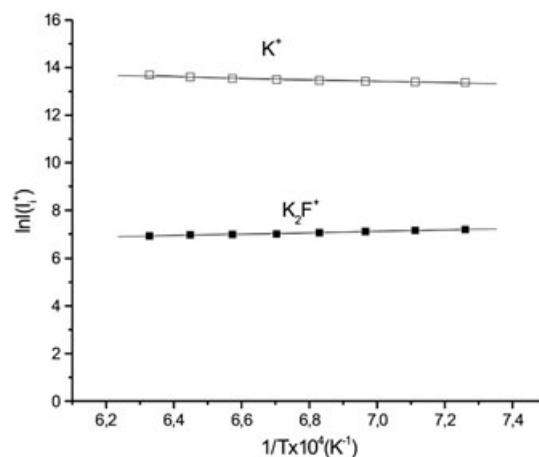
The experimental conditions for measuring the ionization energies of the dipotassium monohalides were optimized by adjustments of the temperatures of the filaments. The $K_2X^+$ ion intensities changed exponentially with increasing temperature of the central filament. The temperature dependence of the currents ($I_i^+$) of the most abundant isotopes of $K_2F^+$, $K_2Cl^+$, $K_2Br^+$ and $K_2F^+$ are presented in Figs. 3–6, respectively.

The ionization energies were determined from the slopes of the plots (Figs. 3–6) and compared with the known ionization energy of the reference ion. The ionization energies for $K_2X^+$ (X=F, Cl, Br, I) are presented in Table 1, together with the IE values for $Li_2X^+$ (X=F, Cl, Br, I).
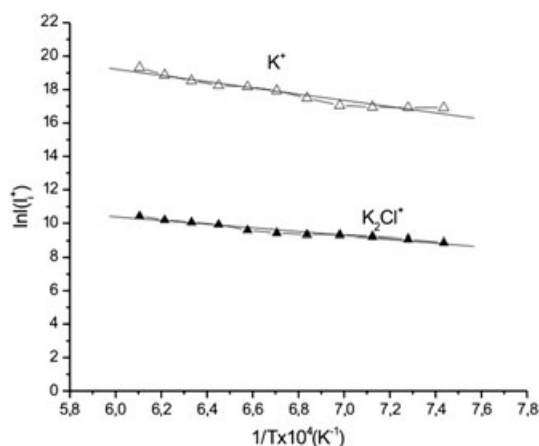
The ionization energy of $K_2Cl$ presented in Table 1 agrees with previous experimental data obtained by photoionization mass spectrometry,[26] which implies that this method is appropriate for studying small dipotassium monohalide clusters.

**Table 1.** Experimental values of ionization energies (IE) for clusters: $K_2X^+$ and $Li_2X^+$ (X=F, Cl, Br, I)

| Ion | IE (eV) this work | Ion | IE (eV) previous work[46,47] |
|---|---|---|---|
| $K_2F^+$ | 3.83±0.1 | $Li_2F^+$ | 3.8±0.1 |
| $K_2Cl^+$ | 3.68±0.1 | $Li_2Cl^+$ | 3.8±0.1 |
| $K_2Br^+$ | 3.95±0.1 | $Li_2Br^+$ | 3.9±0.1 |
| $K_2I^+$ | 3.92±0.1 | $Li_2I^+$ | 4.0±0.1 |

and 0.05 for $m/z$ 113, 115 and 117, respectively, agree with those calculated for $K_2Cl$. The signals at $m/z$ 113, 115 and 117 correspond to different isotopic combinations in $K_2Cl$; i.e. $m/z$ 113 for $^{39}K_2^{35}Cl$, $m/z$ 115 for $^{39}K^{41}K^{35}Cl$ and $m/z$ 117 for $^{39}K^{41}K^{37}Cl$. Peaks at $m/z$ 97 (100%), 99 (14.4%) and 101 (0,5%) correspond to different isotopic combinations in $K_2F$; i.e. $m/z$ 97 for $^{39}K_2^{19}F$, $m/z$ 99 for $^{39}K^{41}K^{19}F$ and $m/z$ 101 for $^{41}K_2^{19}F$. The signals at $m/z$ 157 (89.3% of $^{39}K_2^{79}Br$), 159 (100% of $^{39}K_2^{81}Br$ or $^{39}K^{41}K^{79}Br$) and 161 (13% of $^{39}K^{41}K^{81}Br$ or $^{41}K_2^{79}Br$) are assigned to $K_2Br$. The signals at $m/z$ 205 (100% of $^{39}K_2^{127}I$), 207(14.4% of $^{39}K^{41}K^{127}I$) and 209 (0.5% of $^{41}K_2^{127}I$) correspond to $K_2I$.

A conceivable model of TIMS in obtaining ions of $K_2X$ clusters of potassium halides is the decomposition of a part of KX (i.e. part of the KX decomposes into $K^0$ i $X^0$, and then ionizes to form $K^+$ and $X^-$; $K^+$ combines with non-decomposed KX to form $K_2X$). Another possible process could be the dissociative ionization of $K_2X_2$. The stoichiometric dimer ($K_2X_2$) is one of



**Figure 3.** Plots of ln(ion current) versus 1/T for: $K_2F^+$ and K.

**Figure 4.** Plots of ln(ion current) versus $1/T$ for: $K_2Cl^+$ and K.



**Figure 6.** Plots of ln(ion current) versus $1/T$ for: $K_2I^+$ and K.

The excess-electron clusters $M_2X$ of potassium halides and lithium halides show different behavior with respect to stoichiometric cluster type $M_2X_2$. The values of the ionization energies of the $K_2X$ and $Li_2X$ clusters (Table 1) ~4.0eV suggest that they belong to the group of F-center clusters, where the excess electron takes the place of the missing halogen atom.
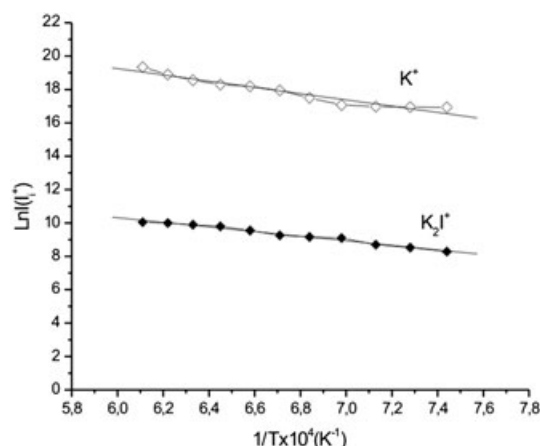
The IE values of $K_2X$ (here X=F, Cl, Br, I) are lower than that of the potassium atom (4.34eV). It has been concluded that $K_2X$ belongs to the group of 'superalkali' species in which the odd electron is delocalized over two potassium atoms.[21] Similar behavior was found for similar clusters containing lithium in a previous study.[46,47]

The IE values obtained for the $K_2X$ clusters are lower than the ionization energy for the $K_2$ cluster ($4.05\pm0.05$eV),[49] which means that the presence of a halogen element lowers the ionization energy of metal clusters. The $K_2Cl$ ionization energy is the lowest in the group of dipotassium monohalide clusters.

The IE of $Li_2X$ slightly increases with increasing electron affinity of the halogen, i.e. in the order of F, Cl, Br and I. However, the experimentally determined ionization energy trend $IE(K_2Br) > IE(K_2I) > IE(K_2F) > IE(K_2Cl)$ does not follow the trend of the electronic affinity of halogen elements in the cluster. One should, however, bear in mind that in clusters with nine valence electrons the values of the ionization energies oscillate, but the amplitudes of the oscillations are within the present experimental error.

## CONCLUSIONS

The thermal ionization method in mass spectrometry offers the possibility of the formation of F-center-type clusters such as $K_2X^+$ (X=F, Cl, Br, I), and the measurement of their ionization energies.

The present paper is the first to report experimentally obtained values of ionization energies of $K_2X$ (X=F, Br and I). The behaviors of the $K_2X$ and $Li_2X$ systems are similar; they have similar ionization energies, depending on the type of halogen atom and they both belong to the group of 'hypervalent' species in which the odd electron is delocalized over two potassium atoms. However, the experimentally determined ionization energy trend for $K_2X$ clusters does not correspond to the trend for $Li_2X$ clusters (X=F, Cl, Br, I). On the other hand, in clusters with nine valence electrons the values of the ionization energies oscillate, but the amplitudes of the oscillations are within the experimental error.

## Acknowledgement

**Figure 5.** Plots of ln(ion current) versus $1/T$ for: $K_2Br^+$ and K.

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