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KINETIC ENERGY MEASUREMENTS OF IONS EMITTED FROM ALKALI HALIDES AND THEIR MIXTURES IN ^{252}Cf PLASMA DESORPTION MASS SPECTROMETRY

U. K. ABEYWARNA*, R. A. ZUBAREV+, P. HÅKANSSON AND T. R. ARIYARATNE#

Division of Ion Physics, The Ångström Laboratory,
Uppsala University, Sweden

ABSTRACT

Kinetic energy measurements of both positive and negative ions emitted from several alkali halides and their mixtures are reported. The measurements were conducted using the energy cut-off property of the ion mirror of a reflector type ^{252}Cf plasma desorption mass spectrometer. The results obtained indicate that some fraction of the desorbed ions emitted under ^{252}Cf bombardment have a kinetic energy deficit compared to the ions which gain full kinetic energy during the acceleration region. The initial kinetic energy of a particular ion was found to be rather independent upon the sample composition.

1. INTRODUCTION

Kinetic energy measurements are directly related to the dynamics of the ion formation. Therefore, the kinetic energy measurements are very useful for understanding the desorption process which is not fully revealed so far. After the invention of Plasma Desorption Mass Spectrometry (PDMS) by Macfarlane and co-workers in 1974[1], absolute kinetic energy measurements were carried out in several groups. The absolute energy distributions or the mean absolute kinetic energy values have been obtained using the linear type mass spectrometer[2-5]. In the absolute method, the results strongly depend on the relevant system parameters which should be known or measured very accurately[4]. The present method has been previously used in studying kinetic energy distributions of small ions[6] and molecular ions[7] desorbed by a laser. The approach utilises the energy cut off property of a reflector and hence there is only a small dependence of the spectrometer parameters. The extracted energy values can only be compared relatively among the ions in the same sample as the point corresponding to zero energy is not known. The method is hence called the "relative energy measurements". Apart from measuring the relative energy variations or the energy distributions, this method can be used for comparison with the energies of the absolute method if the same sample is used in both cases. This is important since the initial kinetic energy data are rather scarce in the literature.

2. EXPERIMENTAL

The measurements were made using one of the reflecting time-of-flight mass spectrometers at the Uppsala University, Sweden. The schematic diagram of the instrument is shown in Fig.1. For these experiments, spontaneously emitted fission fragments of a ^{252}Cf source are used as primary particles. The sample deposited onto a

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* Department of Physics, University of Kelaniya, Kelaniya, Sri Lanka
+ Box 91, Baker Chemistry lab, Cornell University, Ithaca, NY 14853, USA
# Department of Physics, University of Colombo, Colombo, Sri Lanka

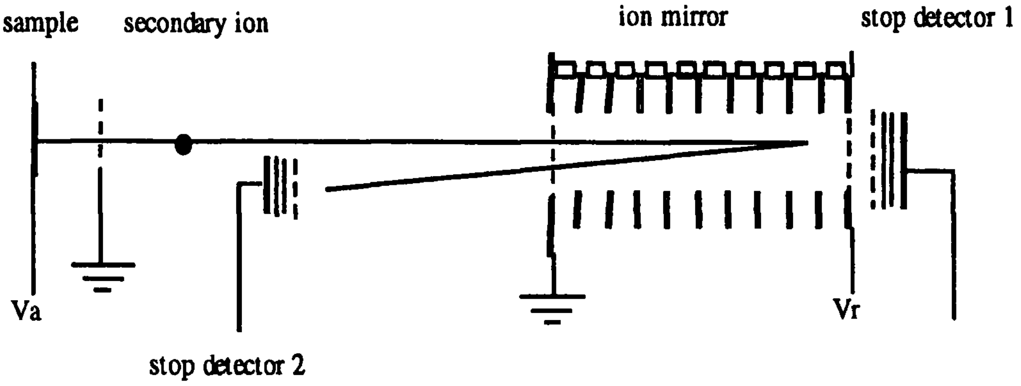

Fig. 1. Schematic diagram of the time-of-flight mass spectrometer

thin film, is bombarded from the back side. The secondary ions which are desorbed from the sample are first accelerated by an electric field between the target, which is kept at high voltage (12 kV) and a grounded grid placed 5 mm away. Then the ions enter into the field free region and later on they are reflected by an uniform electrostatic field in a single stage ion mirror[8]. The reflected ions are finally detected by a micro channel plate detector (stop detector 2). The total equivalent length of the flight path is nearly 2 m. Salt and salt mixtures were used desolved in trifloroacetic acid (TFA) as samples. In order to obtain a fairly good homogeneous surface, the targets were spin-coated onto an aluminised mylar backing[9].

As in the experiment done by the Manitoba group[7], the measurements were conducted by varying the acceleration voltage(V_a) from -45 V to +45 V relative to the reflector voltage(V_r). Initially V_r was higher than V_a and almost all the ions are reflected by the electric field and reached the stop detector. In the course of the experiment, V_a was changed stepwise by 3 V, so the ions having higher kinetic energy penetrated the grid at the rear side of the reflector and the amount of the detected ions were gradually decreasing. The data acquisition required several spectra of the same sample at different V_a to be obtained. In the analysis, the intensities (or areas) of corresponding ion peaks were measured and plotted as a function of the voltage difference V_r-V_a, giving the so called integral energy distribution. In this work, the sum of the three most prominent channels was used as the intensity of an ion peak. It was noticed that the intensity of the peaks dropped faster and more radically than the peak area. On the other hand, the width of the peaks increased, and a tailing part on the low time-of-flight (TOF) side of the peaks appeared at low values of V_a. In these occasions, the areas of the peaks couldn't be measured accurately. Another important consideration is that only the stable ions are taken into account by measuring the intensity of the peaks, while peak areas also include products of metastable fragmentation of ions.

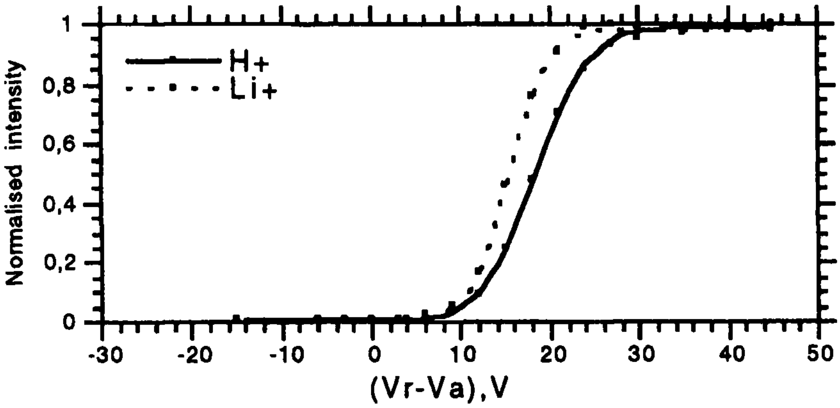

Fig. 2. Normalised intensity variations of H+ and Li+ ions as a function of the voltage difference V_r -V_a

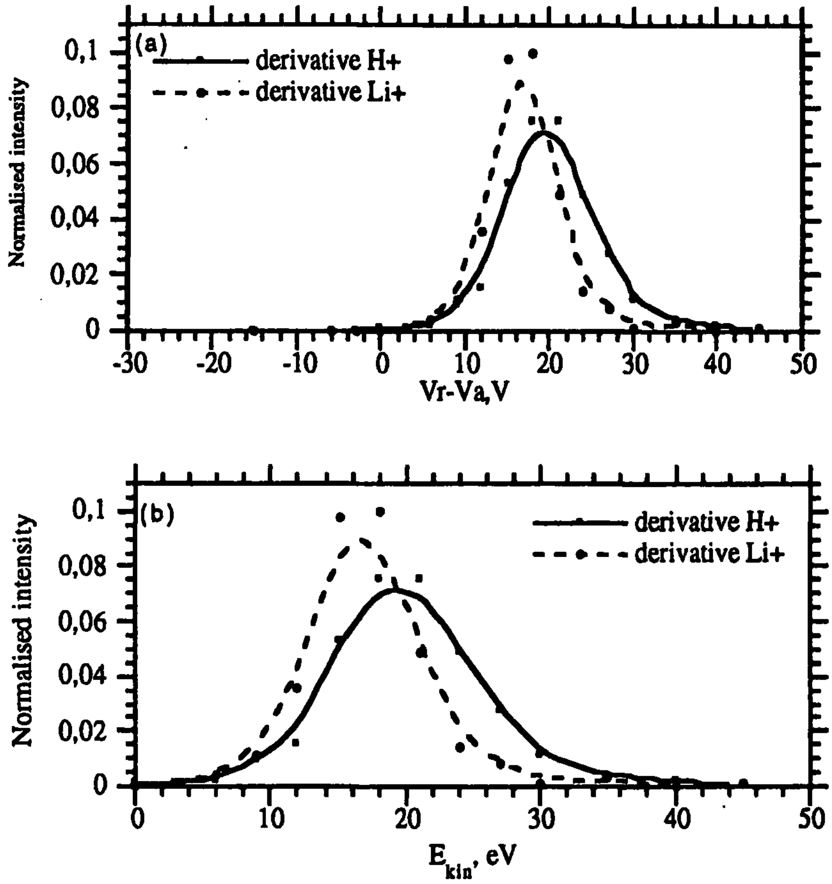

Fig. 3. (a) non-calibrated (b) calibrated (in absolute units) kinetic energy distributions of H^+ ions and Li^+ ions

Fig.2 shows typical integral curves obtained for H^+ and Li^+ ions from a sample of salt mixture (LiCl, NaCl and CsBr). Differentiation of the above curves results in the non-calibrated kinetic energy distributions shown in Fig.3(a). Fig.3(b) represents the calibrated kinetic energy distribution in absolute units. The centroid of each distribution gives the kinetic energy of an ion. In order to convert the voltage difference, $V_r - V_a$, in Fig.3(a) to a initial kinetic energy in Fig 3(b) it is necessary to calibrate $V_r - V_a$. Therefore it is required to know the absolute kinetic energy value of at least one ion in both positive and negative spectra in the linear method. 6.0 eV and 1.8 eV are taken as the absolute kinetic energy values of positive and negative hydrogen ions respectively[10].

The obtained kinetic energy distributions were not accurate as the integral distributions consisted of a set of discrete points. Therefore an appropriate curve was fitted to the integral distribution directly. The integral of a Gaussion curve (ie: error function) was used when no tailing was observed in the integral distribution. The mean value of the Gaussion distribution was considered as the kinetic energy of an ion. The sum of the integrals of two Gaussian curves was used to extract both the ion kinetic energy and the percentage of the ions having an energy deficit when tailing was present.

3. RESULTS AND DISCUSSION

As shown in Fig. 4, the integral curve for the intensity variation of a peak was shifted on the $V_r - V_a$ scale compared to the area of the peak (yield). This effect is easy to understand if one takes into account that the area of the peak drops only when ions start to penetrate the rear grid of the reflector, while the intensity goes down already when ions approach the grid, since the field inhomogeneity near the grid wires causes broadening of the TOF peaks.

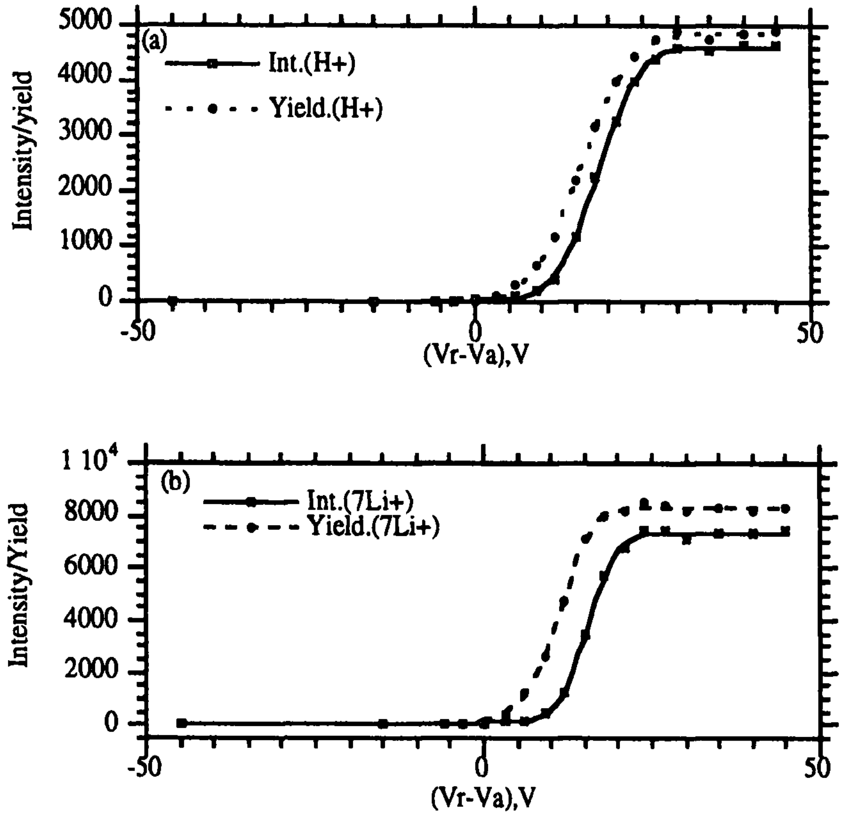

Fig. 4. Variations of the peak intensity and yield as a function of the voltage difference $V_r - V_a$ for (a) H^+ and (b) Li^+ ions

A comparison of the two sets of curves has shown that the only difference was a shift of the zero point. The difference between the kinetic energies was negligible for most ions independent of the used method. The kinetic energy and the percentage of the ions having an energy deficit are presented in Table 1 for a mixture of salt samples based on the intensity measurements.

Table 1: The kinetic energy and the percentage of the energy deficit of positive and negative ions of a sample of salt mixture (LiCl, NaCl and CsBr).

Ion	Kinetic energy, eV	% of energy deficit
H^+	6.0±0.1	0
H_2+	7.0±0.7	0
Li_6^+	3.1±0.2	0.1
Li_7^+	3.1±0.1	0.2
Na^+	4.5±0.1	31.2
Cs^+	6.2±0.1	29.5
H^-	1.8±0.2	0
F^-	4.9±0.1	0.1
24^-	5.1±0.2	0.2
25^-	5.0±0.1	5.4
CN^-	4.7±0.2	19.8
$(LiF)F^-$	5.6±0.2	32.4

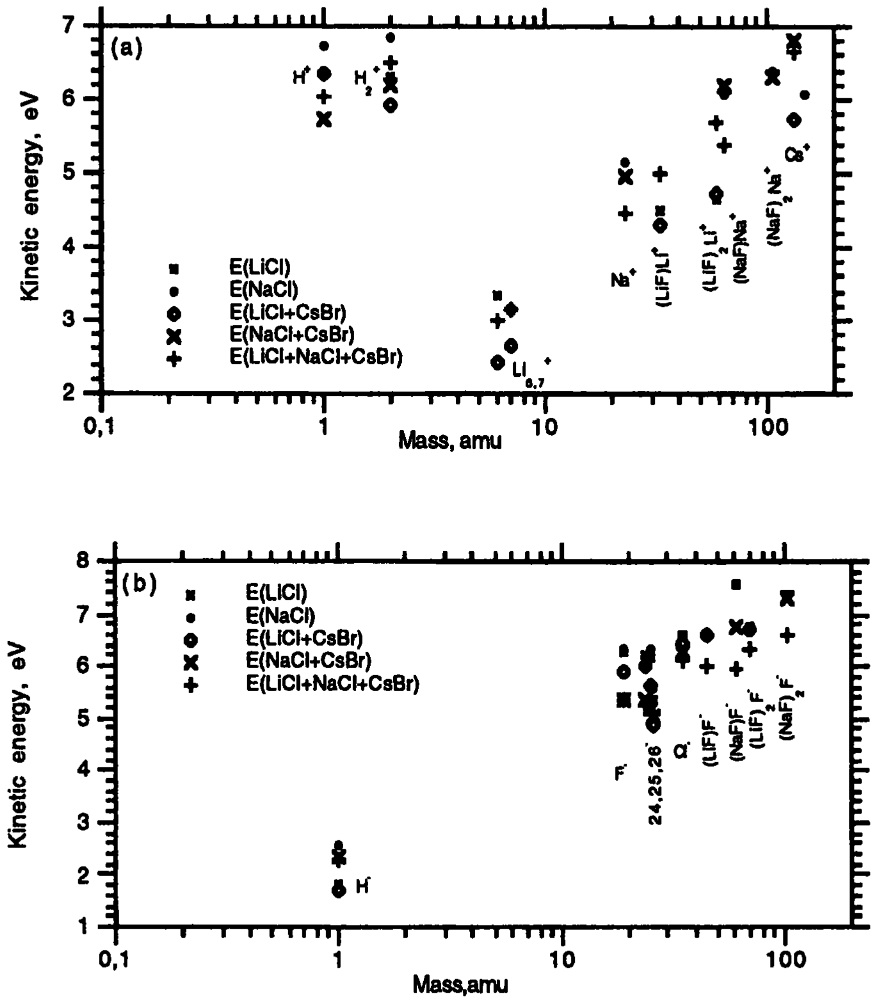

Fig. 5. The mean relative energy of (a) positive and (b) negative ions of alkali halides and their mixtures

Fig.5 represents the positive and negative kinetic energy variations with mass for two different salt samples and three different mixtures of salt samples. It follows from the energy variations of the positive and the negative ions for all samples in which the kinetic energy variations are independent on the sample composition. The H^+ ion and its cluster ion H_2^+ in positive spectra have more or less higher kinetic energy values while the H^- ion in negative spectra has the lowest kinetic energy value compared to all ions in each sample. Shortly after the primary ion hits the sample, a positively charged track is formed[11], repelling the positive ions and attracting the negative ions at once. As the hydrogen ion and its cluster ion have the smallest mass compared to the other ions in the sample and the ejection of the hydrogen ions occur at the initial stage of the desorption process, the positive hydrogen ion and its cluster ion gain most of the energy from the track while the negative hydrogen ion gains least of the energy from the track.

Apart from the hydrogen ions, the kinetic energies of the other positive and negative ions increase slightly with their masses irrespective of the composition of the sample. The kinetic energies are almost the same for the consecutive masses such as H^+/H_2^+ and Li_6^+/Li_7^+ in positive spectra and $24^-/25^-/26^-$ in negative spectra. On the other hand, the kinetic energies of the clusters are not much higher than those of the atomic ions regardless of their masses. The whole kinetic energy range is limited to a few eV.

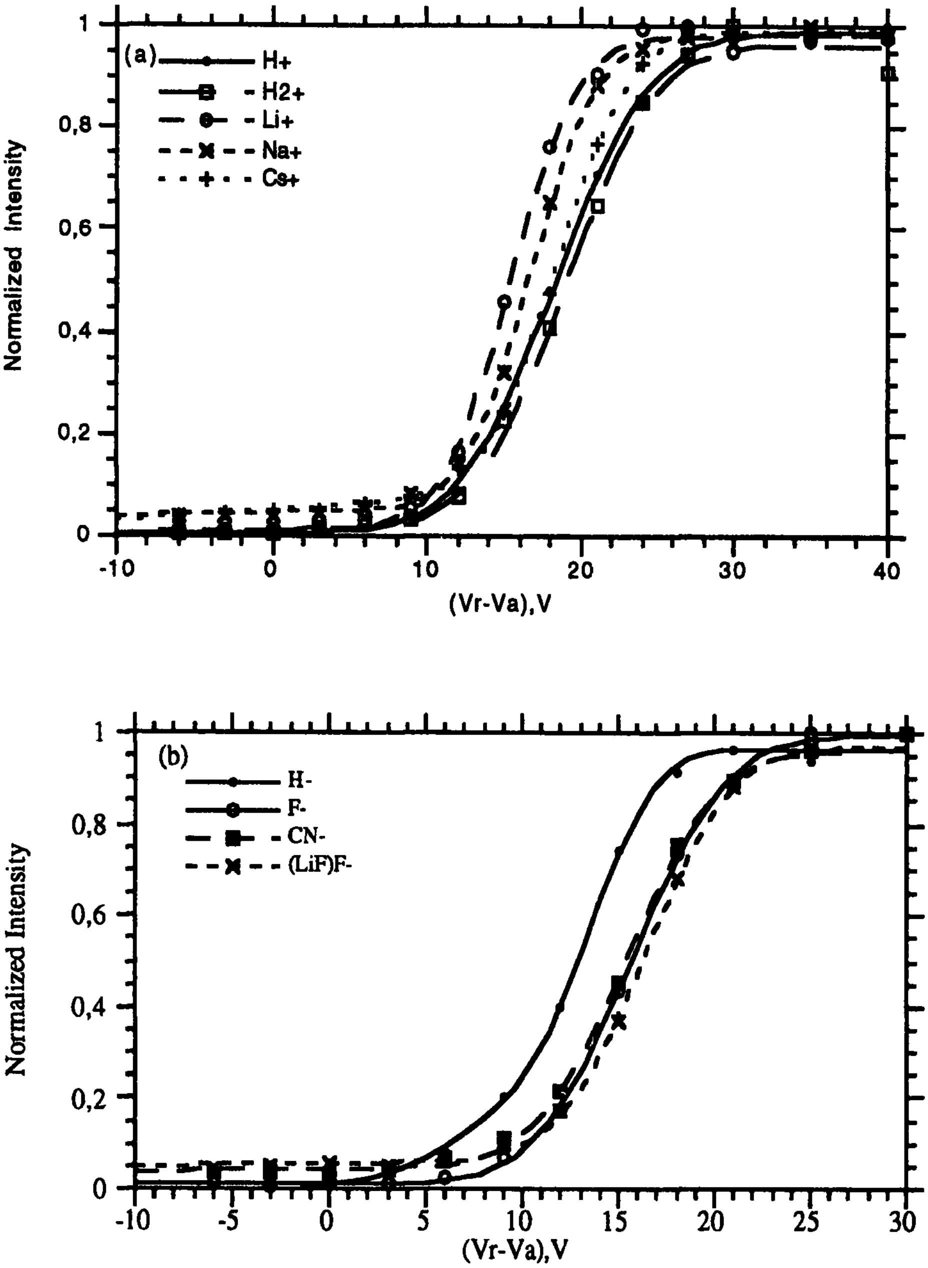

Fig. 6. The normalised intensity variations of (a) positive and (b) negative ions of alkali halides and their mixtures as a function of the voltage difference $V_r - V_a$

In fig.6(a) and 6(b) the normalised intensities are plotted for several peaks in both positive and negative spectra as a function of the voltage difference $V_r - V_a$. When $V_r - V_a > 30$ V the normalised intensities of all ions approach one. However for $V_r - V_a < 0$ it is clearly noticiable that only the normalised intensities of hydrogen and its cluster ions approach zero while the other ions are not. All ions should be able to penetrate the rear grid of the reflector but only the hydrogen and its cluster penetrate totally. Approximately 2- 5% of the normalised intensities of the rest of the ions can be seen when $V_r - V_a = 0$ and their intensities don't drop to zero even at $V_r - V_a = -45$ V. The fraction of ions which shows the energy deficit contributes to a low energy tail in the kinetic energy distribution which can be obtained by differentiating the integral distribution as in the Fig.2. They have gained less kinetic energy than what corresponds to the ions which have gained full energy in the acceleration region. This implies that a fraction of the ions are formed in the gas phase somewhere above the sample surface. The results of kinetic energies and no energy deficits of hydrogen ions verify the specificity of the ejection process of the hydrogen ion compared to other ions emitted from the same sample[12]. Fig.7 shows the energy deficit of Li+ and its cluster ions. It can be seen that the cluster ions also show higher energy deficit than of that of atomic ions.

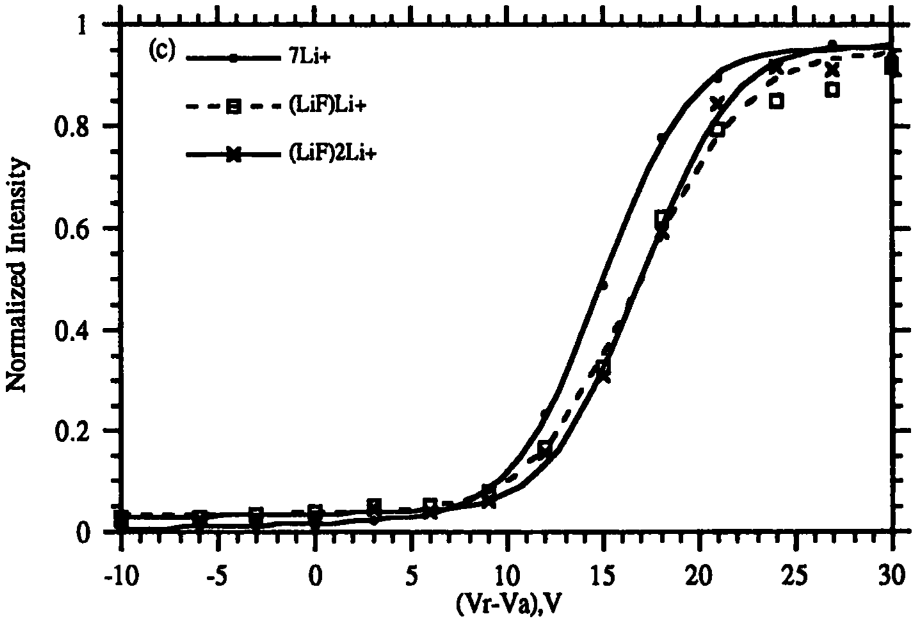

Fig. 7. The normalised intensity variations of Li+ and its cluster ions of alkali halides and their mixtures as a function of the voltage difference $V_r - V_a$

4. CONCLUSION

The relative energy method gives information on the kinetic energy and the kinetic energy distribution relative to the peaks in the same spectrum. This can be used as a comparative method for the absolute energy method since there are very limited energy measurements in the literature. It was found that the kinetic energy of a particular ion was independent upon the sample composition. It is clear that the ejection process of hydrogen ions is different from other ions emitted from same sample. This supports the idea that the positively charged thack is formed initially after the passing primary ions[11]. The kinetic energy distribution having a low energy tail implies that a fraction of the ions shows an energy deficit. They are probably formed in the gas phase during the desorption process.

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