

LASER PHOTOIONIZATION OF POTASSIUM CLUSTERS UP TO  $K_8$

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Some features of small potassium clusters  $K_n$ ,  $n \leq 8$  are investigated in a crossed laser-molecular beams experiment coupled with a time-of-flight mass spectrometer. Abrupt step is found in the mass spectrum for  $n = 8$  when the ionizing wavelength is higher than the ionization potentials. Isotopic composition of each mass is observed. Different behavior in ionization potential spectral profiles between odd-and even-numbered clusters is shown. These effects are interpreted in terms of cluster formation and structures.

INTRODUCTION

The ability to dispose of free clusters with relatively large abundance by using molecular beam technics has improved the possibility of their experimental study. Once

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formed the neutral species may be investigated by electron diffraction. With this method informations on the geometrical structures have been obtained for various Van der Waals species [1, 2]. However, in most cases, mass selectivity is requested for isolated mass diagnostic and this implies a preliminary ionization of clusters: no direct information on neutrals can be achieved. For instance fine structures observed in the relative ion intensities of mass spectra have been tentatively related to neutral abundances i. e. to the intrinsic stability of the corresponding neutral clusters [3-5]. But this is still subject to controversy since these intensities are strongly dependent on ionization cross-section, on the puzzling fragmentation paths and even on the energy of the ionization source. When this later can be varied, spectroscopic studies lead to more reliable information on geometrical and electronic structures with the cluster size. Up to now, for metallic clusters, high resolution vibrational structures have been put into evidence for  $\text{Na}_3$  and  $\text{Cu}_3$  species only [6, 7]. More extended results have been obtained in the knowledge of the photoionization efficiency (P.I.E.) curves in their threshold region [8-14]. Recent developments relate to inner shell autoionization spectra of  $\text{Hg}_n$  clusters [15]. For these experiments several types of cluster source are used-supersonic molecular beams [8-10, 13, 15], seeded beams [11, 12, 14] - laser vaporization [12] - whereas ionization is achieved by using electrons [9, 10] or photons - U.V. spectral lamp [8, 11, 14], tunable laser [12, 13] or even synchrotron radiation [15].

The work reported here deals with results obtained on small potassium clusters  $K_n$ ,  $n \leq 8$  in a crossed laser-molecular beams experiment. The main point is the analysis of the threshold behavior of the P.I.E. curves with size, giving rise to informations on the pairing effect for electrons.

#### Experimental set-up

The cluster beam is formed in an adiabatic expansion of pure potassium vapor through a 100  $\mu\text{m}$  diameter nozzle. The metal is vaporized in a two-chamber oven. The stagnation pressure in the oven is typically 300 torr. In order to prevent clogging we used distilled potassium and the nozzle is heated 50°C above the oven temperature. Once formed the neutral species enter a ionization region located about 10 cm downstream from the nozzle. Then they are photoionized by a tunable U.V. laser which crosses the molecular beam at right angles. The laser source consists of a pulsed tunable dye laser (15 Hz repetition rate, 10 ns pulse width) using the coumarin 540 A or 500 pumped by the third harmonic of a Quantel YAG laser. After two amplifying stages the green-yellow beam is frequency mixed in a tilted KDP cristal with the fundamental frequency of the pump laser (1.064  $\mu\text{m}$ ) in order to generate radiation in the 340 - 380 nm range. This wavelength domain is suitable for one-photon ionization of small potassium clusters  $K_n$  ( $3 \leq n \leq 8$ ) in their threshold region [13]. The resulting laser bandwidth in the U.V. range is 10 GHz. An absolute calibration is achieved with a 2 m focal

length/grating spectrometer. Photoions are mass selected using a

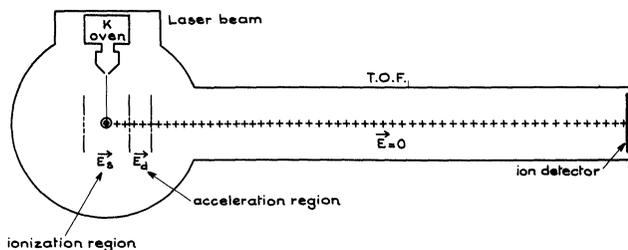


FIGURE 1 Basic-elements of the experimental set up. Typical values of the  $\vec{E}_s$  and  $\vec{E}_d$  fields are 200 V/cm and 1.13 kV/cm respectively. Perpendicular arrangement as shown here is preferred when no pollution of the detector is required.

time-of-flight mass spectrometer (TOFMS). Our set-up allows us to arrange the molecular beam either perpendicularly to both the laser beam and TOFMS axis or on-line with the TOFMS. The mass spectrometer is similar to the three-grid system described in ref. [16]. As shown in the fig. 1, the ions are formed in a low-field ionization region and then accelerated in a second region. A series of constant electric fields and electrostatic lenses focuses the ion beam on a collector (electron multiplier) at the end of a 1.7 m drift tube. Such a system offers the advantage to improve both the ion signal intensity by focusing effect and the over-all resolution by reducing the initial space and kinetic energy distributions. Mass resolution as high as 700 may be achieved. The data

acquisition is obtained by using either box-car averager (PAR 165 model) or a fast multichannel analyser (the 3500 SA Le Croy system).

### Mass spectra

A typical mass spectrum is shown on the Fig. 2. The high resolution is put

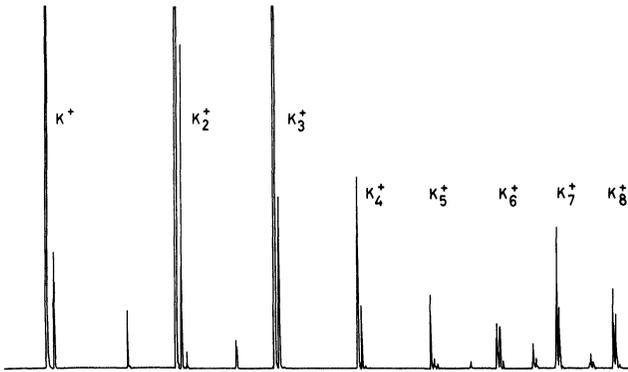


FIGURE 2 Typical TOF mass spectrum as observed with a stagnation pressure of 300 torr at  $\lambda_{UV} = 360$  nm. Such a record is obtained by using a 10 ns - gated boxcar averager. The flight time for  $K^+$  is 18  $\mu$ s. The real intensities for  $K^+$  and  $K_2^+$  are not to scale. Notice the existence of mixed clusters  $Na K_n^+$  corresponding to the unlabelled peaks, the sodium being present as impurity in the potassium.

into evidence by the observation of well resolved isotopic pattern displayed in detail for clusters ( $n \geq 3$ ) on the

fig. 3. In fact the relative intensities in successive masses of ionized species are sensitively varying with the laser wavelength [13]. Despite these variations some constant features may be attributed to properties of neutrals.

With the stagnation pressure and thin nozzle we used here, only relatively small clusters, up to  $K_8$ , are formed in the adiabatic expansion. This is not surprising since a third body is necessary to remove the excess energy of the nucleation process. In our case this role is played by the atomic potassium itself on the contrary with seeded beam for which a high pressure foreign gas is involved. Actually instead of a smooth decay in intensities of increasing masses, one observes an abrupt drop at  $n = 8$ . Such a result has been already mentioned by W.D. Knight and Coll. who used a seeded beam source, in mass spectra of sodium, potassium and mixed clusters [17]. They understood their observations in terms of shell-closing number in a one-electron shell model [18, 19]. In a shell structure model, the work function takes a maximum when a shell is completely filled (here the "p" one in the "s", "p", "d" etc... ordering). This point of view is in contrast to the explanation of "magic numbers" on the basis of structural packing patterns evoked for noble gas and metallic clusters [3, 4].

The other interesting feature deals with isotopic ratios within a given mass. This parameter appears

n \ p	p			
	0	1	2	3
3	1	0.24	0.02	
	1	0.22	0.02	
4	1	0.32	0.03	
	1	0.30	0.03	
5	1	0.46	0.06	
	1	0.37	0.05	
6	1	0.44	0.09	
	1	0.44	0.08	
7	1	0.54	0.12	0.02
	1	0.52	0.11	0.01
8	1	0.60	0.14	0.02
	1	0.59	0.15	0.02

TABLE I Experimental and calculated isotopic abundance for  $K_n^{(n-p)39, p41}$  clusters: for each n value the upper line corresponds to experimental values, the lower line to calculated ones. The relative intensities are normalized to the intensity of the  $K_n^{n39}$  isotope.

insensitive to the one-photon ionization wavelength, except for the couple ( $K^+$ ,  $K_2^+$ ) for which the isotope-shift is frequency resolved by our narrow bandwidth tunable laser. For the clusters, tight vibrational structures hinder any isotopic discrimination. On the table I are given the relative abundances of the main isotope ( $> 1\%$ ) which are present in the  $K_n^{(n-p)39, p41}$  cluster mass. The calculated values are deduced from the following formula neglecting the contribution of the 40 isotope: abundance of the  $K_n^{(n-p)39, p41}$  isotope =  $C_n^p \cdot \alpha^{n-p} \cdot (1-\alpha)^p$  where  $\alpha = 0.93$  is the natural abundance of  $K^{39}$  and the  $C_n^p$  coefficients correspond to the binomial development. The comparison with experimental values (Fig. 3) show an excellent agreement with calculated values, except for one of the  $K_5^+$  isotopes. This is a good indication that nucleation involves the production of clusters via statistical processes. The same conclusion is valid for fragmentation process, if it exists, which would appear as the reversal process of aggregation.

#### Ionization threshold behavior of $K_n$ clusters, $n = 3 - 8$

We have recorded under the same experimental conditions the ion signal intensity vs the U.V. laser frequency. The corresponding P.I.E. curves normalized to the laser energy are shown on the fig. 4. Since in the frequency

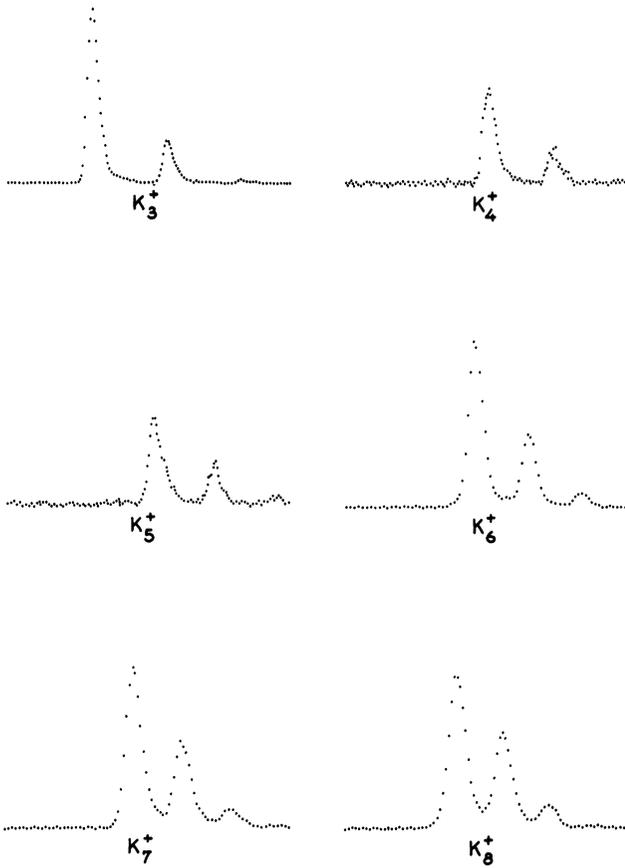


FIGURE 3 Display of isotopic structures for  $K_3^+$  to  $K_8^+$ . This graph has been obtained by using a fast multichannel analyser.

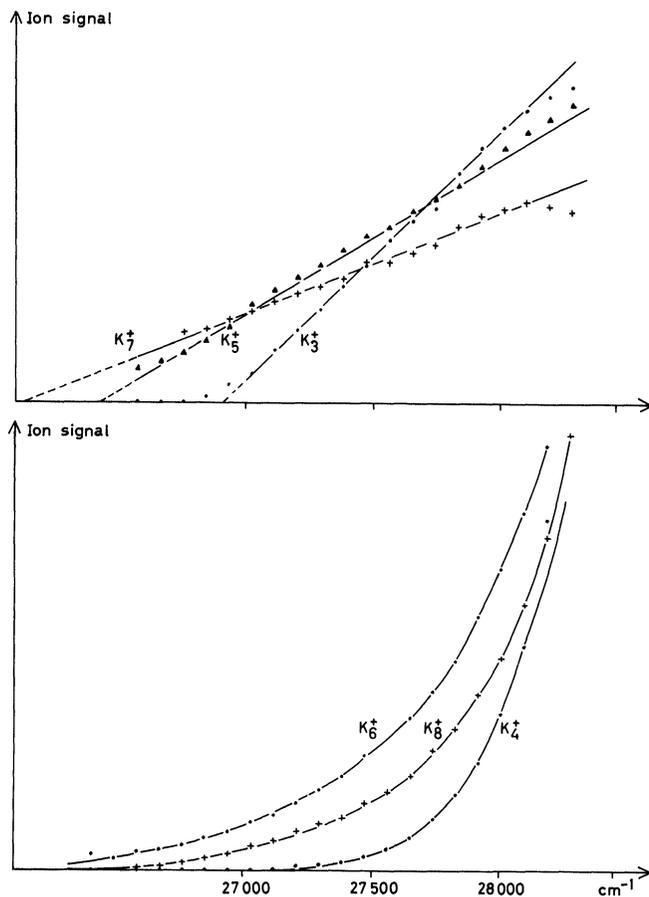


FIGURE 4 Normalized one-photon efficiency curves for the odd and even-numbered  $K_n$  clusters. From the prethreshold region the temperature of  $K_3$  is estimated to be 50 K. Linear extrapolations lead to the A.P.  $E_A(K_3) = 3,34 \pm 0,01$ ,  $E_A(K_5) = 3,28 \pm 0,01$  and  $E_A(K_7) = 3,24 \pm 0,01$  eV.

range of our ionization source only one photon is required to photoionize the  $K_n$  clusters, no fragmentation is expected in the threshold region, due to photodissociation or photopredissociation process of intermediate level. In order to avoid two-photon dissociative ionization we used a reduced laser flux density. In fact no indication of fragmentation effects, which manifest themselves as a slope change in the power law plots of the P.I.E. curves [20] and/or as broadening in the time-profile of the TOFMS peaks [21] was found.

The main feature of the P.I.E. curves is that they exhibit an odd-even alternation. A linear variation is observed for  $K_3^+$ ,  $K_5^+$  and  $K_7^+$ , whereas the P.I.E. profiles for  $K_4^+$ ,  $K_6^+$  and  $K_8^+$  increase much faster than the photon energy. This can be interpreted in terms of Franck-Condon factors. In this frame a linear behavior indicates that they are more or less evenly distributed among the vibrational quantum number, a situation which exists when the equilibrium geometrical structures of neutral and ion are relatively close from each other [22]. On the contrary the quasi-exponential growth for the even-numbered clusters supports the idea of a noticeable change in the equilibrium geometries leading to an increasing of Franck-Condon factors with the vibrational quantum number. This interpretation is in favor of pairing of electrons or dimerization of the neutral even-numbered clusters since in this case the removal of one electron may strongly perturb the covalent bond. Another consequence of such a behavior of P.I.E. curves is that appearance potentials (A.P.) may be deduced via a linear extrapolation for the odd-numbered

clusters. Only an upper limit can be deduced for the even-numbered ones (Fig. 5).

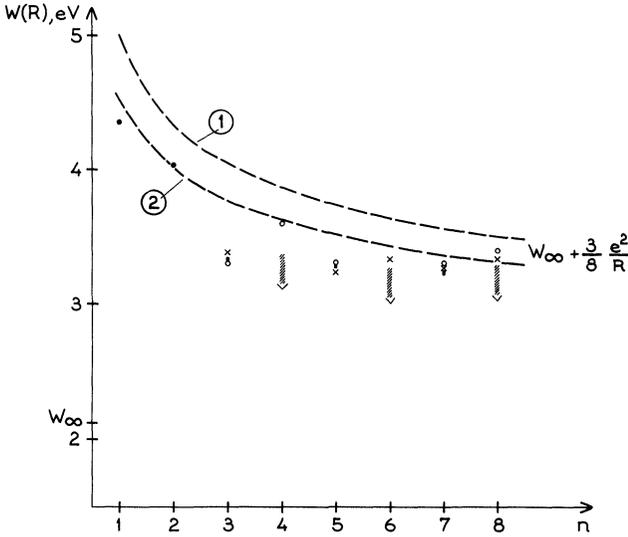


FIGURE 5 A.P. potential determination for  $K_n$  clusters :  
 ■ this work ; × Knigth et al. [14] ; o Schumacher et al. [8]. The dashed lines are calculated from the small metallic sphere picture :  $W(R) = W_\infty + \frac{3}{8} \frac{e^2}{R}$  where  $W_\infty$  is the bulk work function [27a],  $e$  the electron charge and  $R$  the cluster radius taken as  $R_n = r \cdot n^{1/3}$ . For the curve (1)  $r$  is deduced from the diatomic equilibrium distance [28] ; for the curve (2) the nearest neighbor distance in the bulk metal is considered [27b]. The  $n = 2$  value is taken from ref [29].

As it can be seen on the fig. 5, our values are lower than the values obtained from a spherical metallic droplet [23] which predicts a  $1/R$  trend,  $R$  being the droplet radius. This is not surprising since this crude picture is not valid for small clusters. A comparison with the measurements of Schumacher et al. [8] and Knight et al. [14] shows a good agreement for the odd-numbered clusters but a large discrepancy for the even-numbered. The origin of this discrepancy may be found in the broad-band U.V. ionization source they used which requires a deconvolution method for the A.P. determination, in contrast to our laser experiment which leads to a much more direct analysis of the threshold behaviors. This also explains the odd-even alternation in the A.P. values found by Knight et al. [14] which is present in our case only in the shape of P.I.E. curves.

From a theoretical point of view, only the alternation in A.P. values has been considered up to now. This phenomenon is explained as an effect of electron pairing [24-26] but no conclusion can be deduced for the atomic arrangement which can be either a spherical homogeneous - type one [25] or the result of small geometrical structures such as close-packings [26] or dimer units [24].

### CONCLUSION

Despite the fact that some information on cluster formation can be deduced from a simple analysis of the relative ion intensities in mass spectra, more is given by an accurate determination of the P.I.E. curves near

thresholds. They have been observed for the first time free of any apparatus function distortion. Our conclusion is in favour of a non metallic character of small  $K_n$  clusters. However a decisive answer to the non metallic - metallic transition and to the onset of metallic conductivity requires the study of larger clusters. The same conclusion prevails for a test of theoretical models. For instance the spherical-shell structure scheme predicts a large gap for the work function at  $n = 8, 20$  etc... Also interesting is the study of mixed clusters when one or several potassium atoms are replaced by another alkaline atom.

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