# Probing the Electronic Structure of Metal Clusters**

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*Abstract:* The data obtained from photoionization measurements on supersonic molecular beams containing $Na_x$, $K_x$, $NaK_x$, $LiK_x$, $K_xMg$, and $K_xZn$ includes information on neutral species abundances as well as determination of vertical ionization potentials. It is shown that these measurements are incompatible with the present version of the recently proposed spherical shell model (jellium model) of metal clusters.

Recently, there have been several photoionization studies on molecular beams containing alkali metal clusters which have resulted in mass spectra with multimodal cluster ion size distributions[1–3]. It has proven possible to rule out significant fragmentation during or subsequent to ionization as the source of these discontinuous size distributions[4]. Barring major and abrupt changes in ionization cross section as a function of size, it appears probable that the ion distributions observed reflect the abundances of precursor neutrals. In keeping with this interpretation, the data gathered to date for beams of several different alkali metals (and mixtures thereof) using quite disparate experimental arrangements all have in common abundance maxima at $M_2$, $M_8$, $M_{20}$, and $M_{40}$. It has been proposed that these abundance maxima are a measure of enhanced relative thermodynamic stability and that their occurrence is an intrinsic property of s-electron metals[1,2].

It was to explain these observations and associated implications that a statistical model was recently reintroduced[2,5–7,8]. The jellium model describes an alkali metal cluster in terms of a spherically symmetric smeared out positive potential (with charge equivalent to the number of atoms). Electrons are filled into a series of partially degenerate levels which can be determined by solving the simple quantum mechanics of this problem (basically the particle in a three dimensional spherical box). The resulting level filling order – in nuclear nomenclature – is $1s^2$, $1p^6$, $1d^{10}$, $2s^2$, $1f^{14}$, $2p^6$, ... this corresponds to an electron sequence (per filled level) of: 2, 8, 18, 20, 34, 40, ... Interestingly five of the first seven closed shell configurations have valence electron numbers which can be mapped onto the observed maxima. It was shown that closed shell configurations do indeed have local maxima in bond energy per atom[5–7]. However, the magnitude of this relative stabilization is extremely small and can only explain the large maxima observed in the cluster distributions if kinetic effects are also important.

This early success of the model at rationalising abundance maxima in sodium cluster beams in terms of filled shells has since been followed by «observation of electronic shell structure» in potassium cluster beams as well as by measurements on $Na_x$ and $K_x$ which show «some correlation» between cluster polarisability and shell structure[3,9]. These statements appear questionable in the light of the experimental data – missing maxima and monotonically decreasing polarisabilities. We now present further data which is at odds with the jellium model.

Clusters were generated in supersonic molecular beams by expansion of metal vapour(s) from a high temperature oven (typically 750 °C). They were then probed by photoionization mass spectroscopy via irradiation within the ion source of a quadrupole mass spectrometer mounted perpendicular to both molecular and light beams. The radiation source, a 1kW Xe/Hg arc lamp, was combined with a monochromator for ionization potential determinations[10,11].

Table 1 shows ionization potentials (*IP*s) determined for potassium clusters. We report the numbers to a precision of ± 0.1 eV because of undefined isomer and temperature effects. *IP* determinations for alkali metal dimers using the same experimental set up and deconvolution procedures have been shown to have a precision better than ±0.03 eV[10]. The data for potassium clusters as well as an analogous set obtained for sodium clusters show a monotonically decreasing trend – with increasing particle size – towards the bulk work function[4]. Measurements can be well correlated with a simple classical model which regards an alkali metal cluster as a uniform conducting spherical drop. The energy required to move an electron from the surface of such a drop to infinity is related to its curvature (which is in turn related to its size) via $1/R$ where $R$ is the radius of a sphere with the same volume as an n-atomic metal cluster[4]. Interestingly *IP* determinations for clusters of non-alkali metals show similar size dependencies. This is well documented in Fig. 1 where we

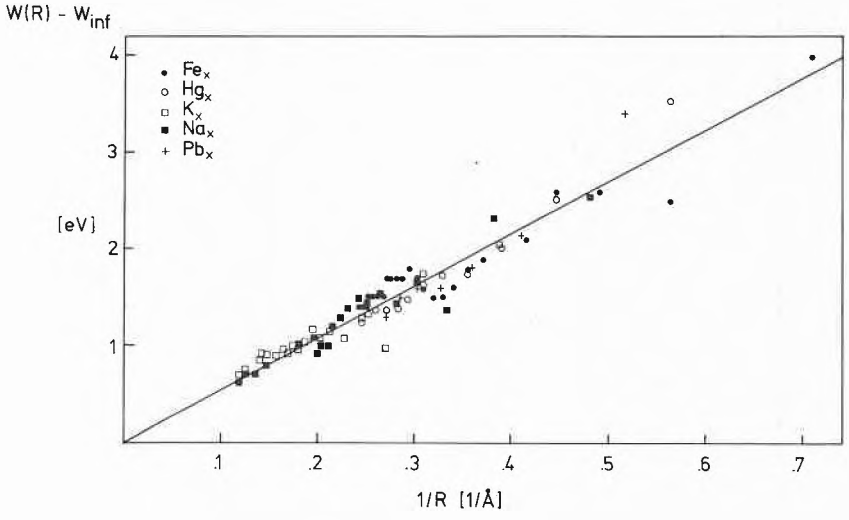


*Fig. 1. «Reduced» ionization potentials for clusters of sodium, potassium, iron, mercury, and lead plotted against 1/R (starting with the atom). R ist the radius of a sphere with the same volume as an n-atomic metal cluster. The straight line results from the classical calculation and has a slope of $(3/8)e^2/R$ (cf. text).*

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***Acknowledgement:* We thank the Swiss National Science Foundation for financial support of this work (grant No. 2.617.82).

plot experimentally determined «reduced» ionization potentials against $1/R$ [12] for clusters of Na, K, Fe, Hg, and Pb. The continuous line corresponds to the classical model.

Table 1. Ionization potentials of potassium clusters [a].

| $M_x$ | *IP* | $M_x$ | *IP* |
|---|---|---|---|
| K | 4.34 | | |
| $K_2$ | 4.0637(2) | $K_{11}$ | 3.30(10) |
| $K_3$ | 3.3(1) | $K_{12}$ | 3.25(10) |
| $K_4$ | 3.6(1) | $K_{13}$ | 3.28(10) |
| $K_5$ | 3.4(1) | $K_{15}$ | 3.21(10) |
| $K_6$ | 3.44(10) | $K_{19}$ | 3.23(10) |
| $K_7$ | 3.40(10) | $K_{20}$ | 3.23(10) |
| $K_8$ | 3.49(10) | $K_{21}$ | 3.16(10) |
| $K_9$ | 3.40(10) | $K_{28\pm1}$ | 3.05(10) |
| $K_{10}$ | 3.27(10) | $K_{34\pm1}$ | 3.01(10) |

[a] All numbers (*IP* values) are in eV; experimental uncertainties in the last decimal place are given in parentheses.

There have been several calculations of alkali metal cluster ionization potentials based on a jellium description [5,6]. In all cases strongly oscillatory behaviour (as a function of size) is predicted with discontinuities at the shell closings – in some cases larger than 1 eV. Fig. 2 shows the predictions of reference [5] together with our determinations for clusters of sodium and potassium. Note that we have not determined an *IP* for each cluster within the size range plotted due to low abundances of the missing clusters. However, the extent and precision of our data sets is sufficient to show that they are fundamentally incompatible with the predictions of the jellium model.

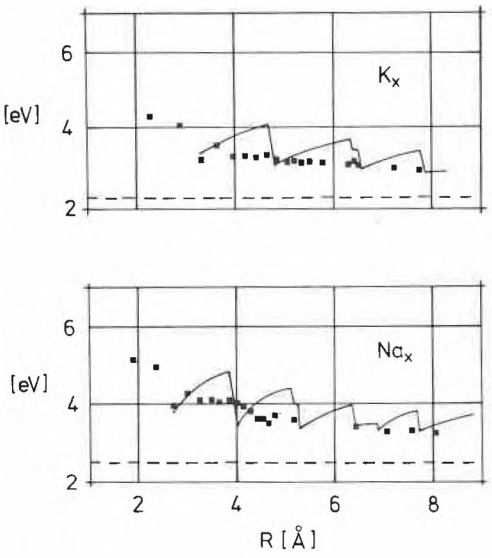


*Fig. 2. Comparison of ionization potentials determined experimentally with the predictions of a self-consistent jellium calculation* [5].

Probably the most serious shortcoming of jellium calculations is their complete neglect of structure and packing. We have attempted to separate electronic and geometric effects in alkali metal clusters by «probing» with heteroatoms which have more than one valence electron per core added to the jellium [13]. In terms of the jellium model, a magnesium atom added to a potassium cluster large enough to allow for Mg participation in bonding, should contribute two electrons. Consequently, if cluster structure were unimportant we would expect to see maxima for clusters with total electron numbers of 8,20,40... (8 electrons corresponds to $K_6Mg$). Instead, Fig. 3 shows that for a mixed expansion of potassium with magnesium we observe an abundance maximum (among magnesium containing species) at $K_8Mg^{\oplus}$. Furthermore, the ionization potential of the more stable $K_8Mg$ (as evidenced by the abundance maximum at $K_8Mg^{\oplus}$) is lower than the ionization potential of the less stable $K_6Mg$ (3.38(10) and 3.95(10) eV) [13]. This is irreconcilable with an electron-only calculation such as the jellium description for which one cannot have less stable molecules with higher ionization potentials.

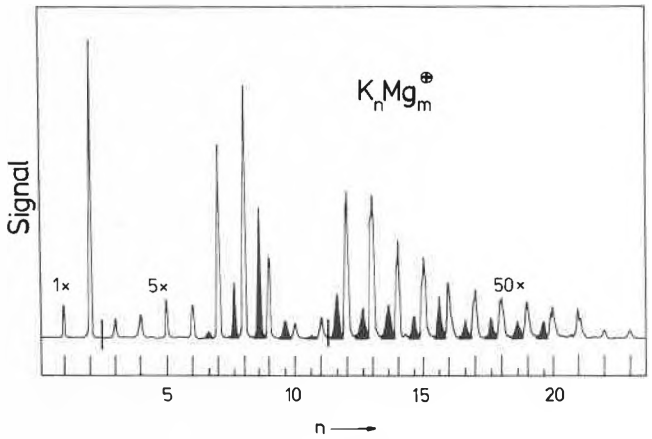


*Fig. 3 Photoionization mass spectrum for a mixed potassium/magnesium expansion. Data were obtained with broad band irradiation from a 1kW Xe/Hg arc lamp. Peaks containing one Mg-atom are shaded.*

While the jellium model served a useful function in pointing out that systematic size-dependent stability variations in alkali metal clusters are related to electronic structure effects, the weight of experimental data now in conflict with its predictions suggests that we need to cast about for a better theoretical description. In contrast to some members of the solid-state physics community involved in metal cluster research, we believe that there is no alternative (or shortcut) to rigorous quantum chemical calculations in this field [14].

Received: June 24, 1985 [FC 20]

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