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Photoionization and shell structure of potassium clusters

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The photoion yields for potassium clusters produced in a supersonic expansion comprising between $N=3$ and 30 atoms are presented. The measured photoionization thresholds show the effects of electronic shell structure, with associated energy gaps in the range 0.1 to 0.3 eV. Odd-even alternations in the yields and thresholds are observed.

The photoionization of metal clusters has been a significant subject of investigation since Foster, Leckenby, and Robbins[1] first measured the ionization potentials for small clusters of alkali-metal atoms. Since then, this work has been extended to larger clusters and other metals by other workers.[2–5]

Observation[6,7] of electronic shell structure[8–10] in alkali-metal clusters has prompted us to extend the range of photoionization experiments on potassium clusters as a means of acquiring further information about their electronic structure. Energy gaps at the major shell closings are implied by the sequence of cluster abundances. We report here on the direct observation of energy gaps seen in a series of ionization profiles for potassium clusters containing between $N=3$ and 30 atoms per cluster. Figure 1 shows the cluster photoion yields as a function of energy, in arbitrary units and normalized to the light intensity. The data for each cluster, except those with $N>21$, are the combined results of several experimental runs, with the stagnation conditions for the supersonic expansion nominally the same for each run ($P_K=4$ kPa, $P_{Ar}=150$ kPa). Error bars derived from counting statistics are shown in each profile. Very recent measurements confirm the thresholds derived from the profiles in Fig. 1. It appears that the odd-even alternations in threshold and post-threshold regions die out between $N=20$ and 30.

The bandwidth of the monchromator used in the experiment was 12 nm. Even at such broad resolution there are observable regular features in the data. For instance, there is a noticeable peak in the yields of each of the even clusters, while the odd cluster yields show a more gradual slope at threshold and less prominent peaks. The approximate energies of the peaks are 3.8 eV for $N=5$–8, 3.5 eV for $N=10$–20, and 3.3 eV for $N=24$–30. In addition, the yields of many of the odd clusters show a shoulder, which is not found in the even cluster profiles, on the low-energy side of the peak. This feature may be related to the unpaired electron in the odd clusters.

In Fig. 2 we have redrawn partial profiles for selected even clusters. The shifts of the profiles make evident the energy gaps above the shell closings at $N=8$, 18, and 20. Although all profiles are not shown in the figure, we point out that similar patterns can be seen in both odd and even cluster profiles. The curves were drawn by connecting the data points with a smooth line, and are truncated at high energy.

Determination of the adiabatic ionization energy of a molecule or a cluster from photoionization spectra can be complicated by thermal and final-state effects.[11] Since the observed thresholds are not sharp, even allowing for the breadth of the experimental resolution, it is not appropriate to assume a step function for the threshold, and the conventional step-function–logarithmic-slope analysis is not applicable to the clusters. Instead, we have used a method which treats consistently the homologous series of clusters. We take the threshold to lie at the intercept on the energy axis of a straight line, fitted to the first rise of the profile, and corrected for the effects of finite instrumental bandwidth.[12] Although the bandwidth is too large to investigate fine-structure features of the profiles, it is entirely adequate to survey the trends in the main features. In particular, the relative values of the thresholds are not distorted by this treatment of the data. Figure 3 is a plot of the ionization threshold of each cluster against the number of atoms in the cluster, N. The error bars pertain to the precision of our determination of the threshold, and may not reflect the accuracy of a measurement of the adiabatic ionization energy. For $N=9$, threshold determination is complicated by the presence of a low-energy tail extending from 3.0 to 3.15 eV, which accounts for the large estimated error in that measurement. The large error bars for $N>20$ are a consequence of weak-signal levels.

The approximate size of the energy gap[13] between electronic shells can be deduced from the threshold data, for a restricted range of cluster sizes, by subtracting the ionization energies of neighboring clusters at a spherical shell closing. It is apparent from the figure that the magnitude of the gap between the $1p$ and $1d$ shells is approximately 0.3 eV at $N=8$. Similarly, the gaps above the $1d$ and $2s$ shells are approximately 0.1 eV at $N=18$ and 20, respectively. These are approximately a factor of 2–3 smaller than are those predicted by jellium calculations.[14]

The ionization thresholds show, in addition to the discontinuities resulting from electronic shell structure, a strong asymptotic $1/R$ dependence. Here, R is the radius of the cluster and is equal to $r_sN^{1/3}$, where r_s is the bulk Wigner-Seitz radius and N the number of atoms in the cluster. Such a $1/R$ dependence has been noted before in the ionization of alkali-metal clusters,[2,3] and can be understood in rudimentary terms through a classical model.[15,16] Other more sophisticated variational[8,17] or self-consistent[9,10] calculations also give ionization potentials which follow approximately the classical $1/R$ dependence. Ekardt calculates separately the electrostatic contribution to the total work function and finds a variation which is not as strong as the $1/R$ trend.

There is a consistent odd-even alternation in the measured thresholds of the clusters up to $N=21$. This was not prominent in earlier work on Na clusters,[2,3] where odd-even alternation was apparent only in the thresholds of the small clusters. The amplitude of the alternation (see Fig. 3) is ap-

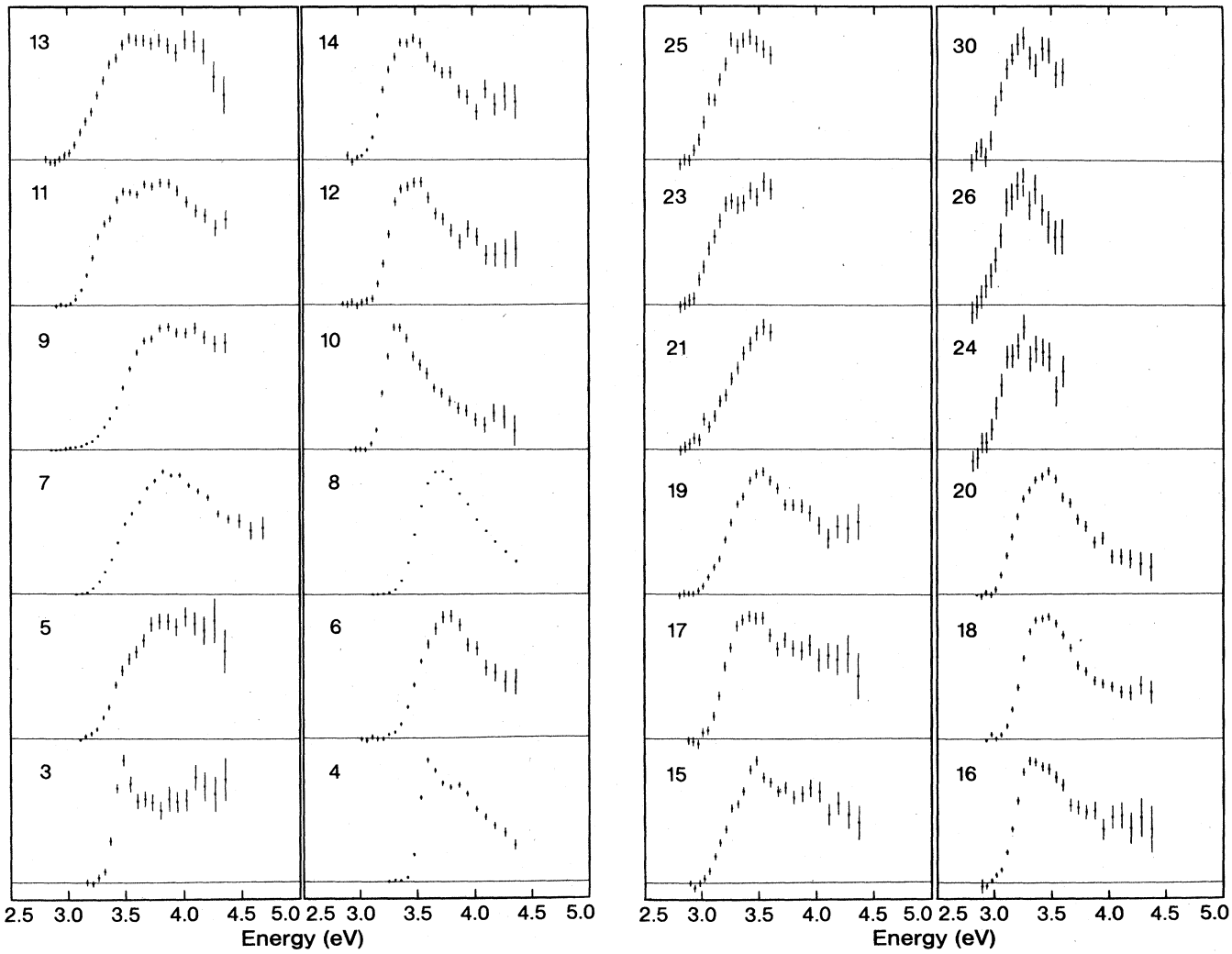

FIG. 1. Photoion yields of potassium clusters with $N = 3$–30 atoms per cluster, plotted against photon energy. The vertical scale is arbitrary.

proximately equal to that predicted by Snider and Sorbello.[18] Their free-electron gas result, when adjusted to $r_s = 5$ for potassium, predicts a jump of 0.07 eV between $N = 10$ and 11, compared with the measured value of 0.14 eV. It is also clear from the data that the magnitude of the alternation decreases with increasing N, as they predict.

The measurements were made using a molecular-beam apparatus which has been described elsewhere.[6] The ionizing light source was a regulated 1-kW xenon lamp whose output was condensed by an $f/0.7$ lens, focused onto the slits of a Czerny-Turner monochromator by an $f/4$ lens. The output of the monochromator was collected and focused onto the cluster beam by another pair of lenses. The monochromator was typically run at a bandwidth of 12 nm as a compromise between resolution and signal strength. A thermopile radiation detector was used to measure the light power, while a photodiode was calibrated simultaneously. The photodiode, because of its much faster response, was used to monitor light intensity during the measurements. Data collection and analysis was done with an LSI-11 computer.

We have not positively determined the extent to which dissociative ionization influences the present results. Although it is possible that it is a relatively frequent occurrence in the production of the observed ions, we do not believe that is the case. We base this belief partly on the observation of strong cluster to cluster variation of the measured static polarizability.[19] If dissociative ionization were a dominant process in the production of the ions, such variation would not be observed. We conclude that if dissociative ionization is occurring, it is not a dominant process.

To summarize, we have found from these measurements direct evidence for electronic shell structure in clusters of a free-electron metal. The thresholds show clear steps at the predicted spherical shell closings, manifesting the electronic degeneracies implicit in a spherical model. In addition there is a regular odd-even alternation in the thresholds and in the shapes of the yield curves. This indicates a general distinction between clusters with paired electrons and those with an unpaired electron.

In future experiments, we will attempt to extend these measurements to higher energies, larger clusters, and other

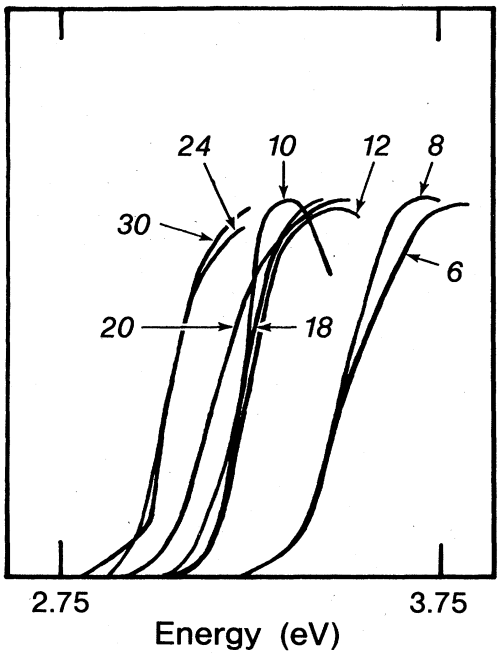

FIG. 2. Superposition of the threshold regions of the yield curves for $N=6$, 8, 10, 12, 18, 20, 24, and 30. Energy gaps resulting from shell structure are in the range 0.1–0.3 eV.

materials in order to determine the range of validity of the shell model. We expect that photoionization measurements on sodium clusters over a sufficiently broad range of cluster sizes will also show clear shell effects. We emphasize that

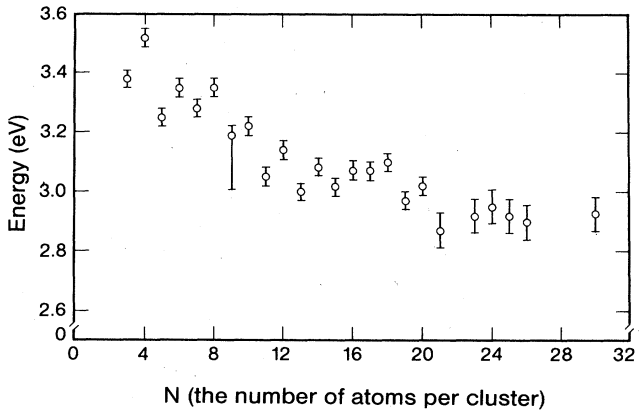

FIG. 3. Measured photoionization thresholds of potassium clusters plotted against N, the number of atoms per cluster. Steps in the ionization threshold at the shell closings are evident.

the observations include peaks in the photoion yield curves which are closely correlated with the shell structure. It, therefore, seems plausible that similar experiments performed at higher resolution may form the beginning of a systematic spectroscopy of the clusters.

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[1]P. J. Foster, R. E. Leckenby, and E. J. Robbins, J. Phys. B **2**, 478 (1969).

[2]A. Herrmann, S. Leutwyler, E. Schumacher, and L. Woste, Helv. Chim. Acta. **61**, 453 (1978); A. Herrman, E. Schumacher, and L. Woste, J. Chem. Phys. **68**, 2327 (1978); Manfred M. Kappes, Roland W. Kunz, and Ernst Schumacher, Chem. Phys. Lett. **91**, 413 (1982).

[3]K. I. Petersen, P. D. Dao, R. W. Farley, and A. W. Castleman, Jr., J. Chem. Phys. **80**, 1780 (1984).

[4]E. A. Rohlfing, D. M. Cox, and A. Kaldor, Chem. Phys. Lett. **99**, 161 (1983); E. A. Rohlfing, D. M. Cox, A. Kaldor, and K. H. Johnson, Chem. Phys. **81**, 3846 (1984).

[5]D. E. Powers, S. G. Hansen, M. E. Geusic, D. L. Michalopoulos, and R. E. Smalley, J. Chem. Phys. **78**, 2866 (1983).

[6]W. D. Knight, K. Clemenger, W. A. de Heer, W. A. Saunders, M. Y. Chou, and M. L. Cohen, Phys. Rev. Lett. **52**, 2141 (1984).

[7]W. D. Knight, W. A. de Heer, K. Clemenger, and W. A. Saunders, Solid State Commun. **53**, 445 (1985).

[8]J. L. Martins, R. Car, and J. Buttet, Surf. Sci. **106**, 265 (1981).

[9]D. E. Beck, Solid State Commun. **49**, 381 (1984).

[10]W. Ekardt, Phys. Rev. B **29**, 1558 (1984).

[11]H. S. W. Massey, *Electronic and Ionic Impact Phenomena,* 2nd ed. (Clarendon, Oxford, 1969), Vol. II, Chap. 14.

[12]P. M. Guyon and J. Berkowitz, J. Chem. Phys. **54**, 1814 (1971).

[13]Clusters other than those at spherical shell closings are subject to ellipsoidal distortions, K. Clemenger, Phys. Rev. B **32**, 1359 (1985), this issue. As a consequence, the energy of the first populated state above a closed shell is depressed, reducing the energy gap to a value below what is given by theories based on a spherical potential.

[14]M. Y. Chou, Andrew Cleland, and Marvin L. Cohen, Solid State Commun. **52**, 645 (1984). See also Refs. 8–10 and D. R. Snider and R. S. Sorbello, Solid State Commun. **47**, 845 (1983); Albert Rose, *ibid.* **45**, 859 (1983).

[15]J. M. Smith, Am. Inst. Aeronaut. Astronaut. J. **3**, 648 (1965).

[16]D. M. Wood, Phys. Rev. Lett. **46**, 749 (1981).

[17]See Snider and Sorbello, and also Rose in Ref. 14.

[18]D. R. Snider and R. S. Sorbello, Surf. Sci. **143**, 204 (1984).

[19]W. D. Knight, K. Clemenger, W. A. de Heer, and W. A. Saunders, Phys. Rev. B **31**, 2539 (1985).