Appl. Phys. B 73, 407–410 (2001)
DOI: 10.1007/s003400100665

Applied Physics B
Lasers and Optics

K. WONG
V. KASPEROVICH
G. TIKHONOV
V.V. KRESIN✉

Photo-ionization efficiency curves of alkali nanoclusters in a beam and determination of metal work functions

Department of Physics and Astronomy, University of Southern California, Los Angeles, CA 90089-0484, USA

Received: 21 June 2001/Revised version: 7 July 2001
Published online: 10 October 2001 •

ABSTRACT We produced free beams of cold nanometer-sized particles of lithium, sodium and potassium and measured the three corresponding photo-ionization yield curves. Quadratic (Fowler) plots, originally developed for bulk surfaces, were found to provide a good fit to the threshold shape and were used to obtain the particle ionization potentials. The latter match precisely the bulk work functions cited in the literature, suggesting that photo-ionization of free nanoclusters may form a useful complement to traditional photoelectron studies of surfaces. Within 0.25–1 eV above the threshold, the ionization efficiency begins to drop. This effect, which has parallels in bulk-surface and small-cluster photoemission, is presently not well understood but may be related to an interplay between electron emission and collective surface plasma excitations.

PACS 79.60.-i; 36.40.Vz

1 Introduction

For decades, the photoelectric effect has served as the paramount method of probing the electronic structure of matter. Both photoemission from bulk surfaces [1] and photo-ionization of atoms and molecules [2] have been studied extensively. In the intermediate size regime, comprised of clusters ranging from a few up to several thousands of atoms, the ionization properties are not as well understood. For alkali metal clusters, a number of research groups have studied the photoelectron spectra and ionization efficiency curves (see, e.g., the reviews in [3–6]). In particular, there has been much work on using the photo-ion yield curves to determine the ionization threshold of neutral alkali clusters as a function of size [7–15]. However, there seems to be no general agreement on the most appropriate method for extracting the thresholds. The more-or-less ad hoc approaches used in the papers cited above include linear or exponential extrapolations and error function fits. The picture is complicated by thermal smearing of the threshold region and by the lack of a general theory of cluster photo-ionization.

In this work, we investigate the photo-ionization efficiency curves for free Li, Na, and K nanoclusters carried in a molecular beam. Photoelectron spectroscopy has been applied extensively to nanoparticles deposited or grown on surfaces [16, 17], but only a few photo-ionization studies on large free clusters have been reported [13, 18, 19]. Our particles are generated in a condensation source cooled to liquid nitrogen temperature; their low internal temperature results in a well-defined threshold shape. As described below, we find that this shape is very well fitted by the quadratic Fowler law derived for bulk surfaces [20]. This form was first used for clusters in a study of large Ag particles [21]. Later, the same group extended their work to several coinage metals [22, 23]. Despite the simplicity and clear physical origin of this method, to our knowledge it has not been applied to alkali clusters.

2 Experimental procedure

An outline of the experimental setup is shown in Fig. 1. Nanoclusters are produced in a vapor condensation source [13, 24–27]. The alkali metal is heated up to a vapor pressure of ≈ 0.1 Torr in a small oven. The vapor travels upwards and is quenched in a flow of cold 99.995% pure He at ≈ 4 Torr, condensing into large cluster particles. The walls of the chamber and the 2.5-mm-diameter nozzle are cooled by liquid nitrogen. Expansion from the nozzle is mildly super-

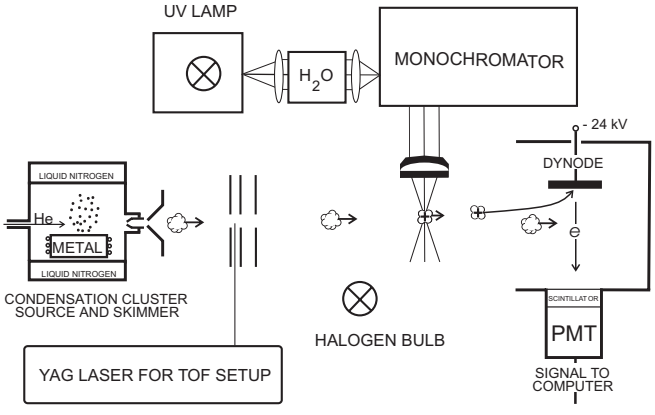

FIGURE 1 Outline of the experimental arrangement (not to scale). A beam of cold alkali nanoparticles is produced in a vapor condensation source and ionized by light from a monochromator. The overall ion yield is detected by a positive-ion detector and counter. A collinear time-of-flight mass spectrometer shows that the particles are in the nanometer size range

✉ Fax: +1-213/740-6653, E-mail: kresin@physics.usc.edu

sonic [28], producing a beam with a narrow ($\approx 10\%$) velocity spread [29]. The particles pass through a skimmer and travel towards the ionization region which is located 2.1 m downstream. A regulated 1 kW Hg−Xe arc lamp is used as the photon source. Its output is passed through a distilled-water filter and focused onto the entrance slit of a monochromator. The slits of the latter are adjusted to a bandpass of 5 nm. The wavelength-selected output was focused onto the cluster beam by a quartz lens. The resulting positively ionized nanoclusters are detected by a Daly dynode-photomultiplier ion-counting arrangement [7, 30]. The light beam is chopped at 147 Hz, and the ion pulses are recorded by a synchronized multichannel scaler. The ion yield is normalized to the photon flux (measured by a calibrated silicon photodiode which can be moved into the spot where the particle and photon beams intersect) and to the nanocluster beam intensity (measured by recording the ion counting rate produced when the beam is illuminated by broadband light from a 100 W halogen light bulb).

The measurements are not size-resolved; however, the fact that we observe well-defined thresholds implies that the particles must be sufficiently large to make size-dependent shifts negligible.

As indicated in Fig. 1, the setup incorporates a linear Wiley–McLaren time-of-flight (TOF) mass spectrometer which can be used to monitor the particle size distribution during the experiment. The TOF spectra suggest average sizes in the range of $R \approx 3$–5 nm ($\approx 2\times10^3$–3×10^4 atoms). However, it is known that pulsed-laser ionization of large metal clusters in the extraction region of the mass spectrometer (in our case, frequency-doubled or -tripled output of a Nd–YAG laser) often produces significant cluster fragmentation (see, e.g., [31, 32]). This is connected with the fact that large cluster cross-sections, in combination with practical laser pulse intensities, easily lead to multiphoton absorption. Furthermore, the secondary-electron emission of the conversion dynode detector decreases with increasing ion mass [33], which suppresses the signal from the heavier side of the size distribution.

The net result of these effects is that the TOF sizes measured here provide only a lower bound; the dominant radii are probably significantly larger, as discussed in the next section. We have, in fact, detected such an effect in an independent measurement of Na nanocluster radius via the size dependence of electron capture cross-sections [29]. Thus the role of the mass spectrometer in the present experiment is not to give an unambiguous determination of particle size, but to monitor the steadiness of particle production in the condensation source.

3 Results and discussion

According to the Fowler law [1, 20] the photoelectron yield near threshold for a bulk metallic surface is given by

$$Y \propto (h\nu - \phi)^2 \,, \tag{1}$$

where $h\nu$ is the photon energy and ϕ is the bulk work function. This formula is derived by evaluating the flux of photo-excited conduction electrons whose momentum is perpendicular to the surface. The effect of surface curvature has been discussed for silver nanoparticles [34]; as expected, for large clusters it is not significant near threshold.

Our data for the three alkali metals Li, Na and K are presented in Fig. 2, where the square root of the measured photo-ionization yield is plotted as a function of photon energy. The nanocluster ionization potential can be extracted from the x-axis intercept according to (1). The results are shown in Table 1. They consistently match the literature values of bulk work functions. The values for Na and K also agree with the experimental [13] and theoretical [3] extrapolations reported in the literature for large clusters. This establishes the fact that the Fowler threshold law (1) provides a good description of the photo-ionization behavior of alkali nanoclusters.

Furthermore, this demonstrates that the technique of cluster beam photo-ionization is a convenient tool for the determination of work functions of materials. Indeed, the high reactivity of alkali metals means that bulk surfaces are easily contaminated, resulting in significant work function shifts [36]. Indeed, "the preparation and preservation of a clean sample surface [is] the main experimental task in photoemission" [37]. The fact that the TOF of a free nanocluster in a beam machine is very short ($\approx 1-10$ ms) can alleviate the bane of contamination and simplify surface spectroscopy.

The measured ionization potentials do not display any significant amount of the well-known $\Delta\phi \approx (3/8)(e^2/R)$ [3,

TABLE 1 A comparison between the nanocluster ionization potentials (IP) determined from a Fowler fit to the ion yield curves and the literature values of bulk surface work functions [35]. The experimental uncertainties are estimated from the scatter in the data

Nanoclusters	Measured IP (eV)	Work function (eV)
Li	2.93 ± 0.05	2.90
Na	2.75 ± 0.05	2.75
K	2.28 ± 0.05	2.30

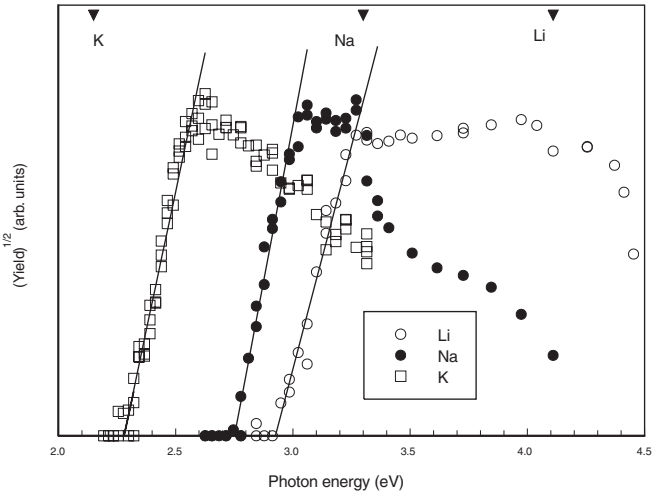

FIGURE 2 The square root of the photo-ionization yield is plotted as a function of photon energy for Li, Na and K nanoparticles. The *straight solid lines* are least-square fits to the data near threshold following the Fowler law (see text). The *triangles* at the top of the graph show the location of the surface plasmon resonance for each metal

4, 38] finite-size shift from the bulk value. As stated at the end of Sect. 2, this implies that the main contribution to our ion signal comes from large nanoparticles ($\gtrsim 5$ nm). Progressively smaller photo-ions will appear as the photon energy increases, but since (i) there are fewer of them and (ii) the photo-ionization cross-section is expected to be proportional to the number of atoms in the system [39], the yield curve near threshold should be dominated by the large species. We performed a calculation for the simple case of a Gaussian size distribution and found that the quadratic shape of the post-threshold region was indeed undamaged. This fact is sufficient for the present analysis, but further size-resolved measurements are needed to clarify and quantify the interrelation between the particle size distribution, the cross-section size dependence, and finer details of the near-threshold behavior of the yield curve.

While the Fowler fit is satisfactory near threshold, it is evident from Fig. 2 that as we go higher in energy all three curves show a drop in ionization efficiency. Similar drops have been observed for the bulk surfaces of Na and K [36, 40] as well as for smaller Na_n clusters [9], K_n clusters [7], positively charged K_n^+ clusters [41] and negatively charged Na_{91}^- clusters [42].

It has been suggested that this feature is related to a coupling between the photoelectrons and the collective surface plasmon resonance [36, 41, 42]. Our data are consistent with the idea of a link between the shape of the ion yield curve and the location of the dipole surface plasmon resonance $\omega_p/\sqrt{3}$ (ω_p is the bulk volume plasmon frequency) [43]. As indicated in Fig. 2, there appears to be a correlation between the position of this resonance and the photon energy at which the ionization curve starts to drop. For both Li and Na, the plasma resonance is located above the work function, and both spectra show a plateau region, which turns into a decrease when the neighborhood of the resonance frequency is reached. Li has a larger separation between the resonance and the work function, and its ionization curve shows a correspondingly longer plateau region before the onset of the drop. For K, on the other hand, the surface plasmon resonance is located below the work function, and the ionization curve shows no plateau at all but begins to drop immediately following the peak of the curve.

The plasmon connection is also consonant with the observation that for bulk alkali surfaces [36, 40] the post-threshold photo-yield peak occurs at frequencies higher than for nanoclusters, in correspondence with the fact that the plasma frequency for a planar surface is higher than that for a spherical particle: $\omega_p/\sqrt{2} > \omega_p/\sqrt{3}$.

Still, the situation is not unambiguous. For example, even independent-electron computations for the self-consistent potential of small and large alkali clusters [44–47] show a photo-ionization cross-section which reaches a maximum and begins to decline. On the other hand, for nanoparticles of coinage metals the yield continues to increase with energy over the entire measured range of > 5 eV [18, 23]. Note, however, that in that case the corresponding surface plasmon resonance [43] is located a full couple of eV below the ionization potential, so its influence may be limited. Obviously, there is a strong need for a fundamental theory of photoemission from finite metal particles and clusters.

4 Summary

We have measured photo-ionization efficiency curves within a range of ≈ 1 eV of threshold for beams of free large lithium, sodium and potassium nanoparticles generated in a liquid nitrogen-cooled condensation source. The observations can be summarized as follows:

- The low internal temperature of the particles results in a well-defined shape of the threshold region. The photo-ionization threshold behavior of metal nanoclusters is well described by the quadratic Fowler shape (1).
- Nanocluster ionization potentials, derived from the Fowler plots, are in excellent agreement with bulk work function values. This suggests that traditional surface photoelectron spectroscopy may be usefully augmented by photo-ionization spectroscopy of nanoparticles of various compositions.
- Following the post-threshold rise, the ion yield curves show a conspicuous drop. There is evidence that this may be related to an interplay between electron emission and collective surface plasma excitations. Such observations highlight the need for deeper experimental and theoretical insights into cluster photo-emission, which is positioned between the relatively well-established realms of molecular and bulk photo-electric effects.

Work to extend the experiments reported here to other alkali metals and to investigate the effect of particle temperature on the shape of the photo-ionization curve is currently in progress in our laboratory.

ACKNOWLEDGEMENTS We are grateful to K. Bowen for very useful comments and for advice on particle source construction. We would like to thank C. Wittig for the loan of equipment, and the staff of the USC Natural Sciences Machine Shop for technical help and skillful machining. This work was supported by the U.S. National Science Foundation.

REFERENCES

1 M. Cardona, L. Ley (Eds.): *Photoemission in Solids* (Springer, Berlin, Heidelberg 1978)
2 J. Berkowitz: *Photoabsorption, Photoionization and Photoelectron Spectroscopy* (Academic, New York 1979)
3 M. Seidl, K.-H. Meiwes-Broer, M. Brack: J. Chem. Phys. **95**, 1295 (1991)
4 W.A. de Heer: Rev. Mod. Phys. **65**, 611 (1993)
5 H. Haberland (Ed.): *Clusters of Atoms and Molecules*, Vols. I and II (Springer, Berlin, Heidelberg 1994)
6 A.W. Castleman, K.H. Bowen: J. Phys. Chem. **100**, 12911 (1996)
7 W.A. Saunders, K. Clemenger, W.A. de Heer, W.D. Knight: Phys. Rev. B **32**, 1366 (1985)
8 C. Bréchignac, Ph. Cahuzac, J.Ph. Roux: Chem. Phys. Lett. **127**, 445 (1991)
9 M.M. Kappes, M. Schär, U. Röthlisberger, C. Yeretzian, E. Schumacher: Chem. Phys. Lett. **143**, 251 (1991)
10 U. Röthlisberger, M. Schär, E. Schumacher: Z. Phys. D **13**, 171 (1988)
11 T. Bergmann, T.P. Martin: J. Chem. Phys. **90**, 2848 (1989)
12 H.G. Limberger, T.P. Martin: J. Chem. Phys. **90**, 2979 (1989)
13 H. Göhlich, T. Lange, T. Bergmann, U. Näher, T.P. Martin: Chem. Phys. Lett. **187**, 67 (1991)
14 Ph. Dugourd, D. Rayane, P. Labastie, B. Vezin, J. Chevaleyre, M. Broyer: Chem. Phys. Lett. **197**, 433 (1992)
15 F. Despa, W. Bouwen, F. Vanhoutte, P. Lievens, R.E. Silverans: Eur. Phys. J. D **11**, 403 (2000)
16 S.B. DiCenzo, G.K. Wertheim: In *Clusters of Atoms and Molecules*, Vol. II, ed. by H. Haberland (Springer, Berlin, Heidelberg 1994) p. 361
17 K.-H. Meiwes-Broer: *Metal Clusters at Surfaces* (Springer, Berlin, Heidelberg 2000)

18 H. Burtscher, H.C. Siegmann: In *Clusters of Atoms and Molecules*, Vol. II, ed. by H. Haberland (Springer, Berlin, Heidelberg 1994) p. 272
19 O. Björneholm, F. Federmann, F. Fössing, T. Möller: Phys. Rev. Lett. **74**, 3017 (1995)
20 R.H. Fowler: Phys. Rev. **38**, 45 (1931)
21 A. Schmidt-Ott, P. Schurtenberger, H.C. Siegmann: Phys. Rev. Lett. **45**, 1284 (1980)
22 H. Burtscher, A. Schmidt-Ott, H.C. Siegmann: Z. Phys. B **56**, 197 (1984)
23 B. Schleicher, H. Burtscher, H.C. Siegmann: Appl. Phys. Lett. **63**, 1193 (1993)
24 K. Sattler, J. Mühlbach, E. Recknagel: Phys. Rev. Lett. **45**, 821 (1980)
25 H. Abe, W. Schulze, B. Tesche: Chem. Phys. **47**, 95 (1980)
26 K.M. McHugh, H.W. Sarkas, J.G. Eaton, C.R. Westgate, K.H. Bowen: Z. Phys. D **12**, 3 (1989)
27 C. Bréchignac, Ph. Cahuzac, F. Carlier, M. de Frutos, A. Masson, J.Ph. Roux: Z. Phys. D **19**, 195 (1991)
28 V. Tarnovsky, M. Bunimovicz, L. Vušković, B. Stumpf, B. Bederson: J. Chem. Phys. **98**, 3894 (1993)
29 V. Kasperovich, K. Wong, G. Tikhonov, V.V. Kresin: Phys. Rev. Lett. **85**, 2729 (2000)
30 W.A. de Heer, W.D. Knight, M.Y. Chou, M.L. Cohen: In *Solid State Physics*, Vol. 40, ed. by H. Ehrenreich, D. Turnbull (Academic, New York 1987) p. 93
31 C. Bréchignac, Ph. Cahuzac, F. Carlier, M. de Frutos, J.Ph. Roux: Phys. Rev. B **47**, 2271 (1993)
32 W. Bouwen, F. Vanhoutte, F. Despa, S. Bouckaert, S. Neukermans, L.T. Kuhn, H. Weidele, P. Lievens, R.E. Silverans: Chem. Phys. Lett. **314**, 227 (1999)
33 B. Spengler, D. Kirsch, R. Kaufmann, M. Karas, F. Hillenkamp, U. Giessmann: Rapid Commun. Mass Spectrom. **4**, 301 (1990)
34 U. Müller, H. Burtscher, A. Schmidt-Ott: Phys. Rev. B **38**, 7814 (1988)
35 H.B. Michaelson: J. Appl. Phys. **48**, 4729 (1977)
36 R.J. Whitefield, J.J. Brady: Phys. Rev. Lett. **26**, 380 (1971)
37 M. Cardona, L. Ley: In *Photoemission in Solids*, ed. by M. Cardona, L. Ley (Springer, Berlin, Heidelberg 1978) p. 1
38 C. Bréchignac: In *Clusters of Atoms and Molecules*, Vol. I, ed. by H. Haberland (Springer, Berlin, Heidelberg 1994) p. 255
39 C. Schmitt, C. Ellert, M. Schmidt, H. Haberland: Z. Phys. D **42**, 145 (1997)
40 N.V. Smith, W.E. Spicer: Phys. Rev. **188**, 593 (1969)
41 C. Bréchignac, Ph. Cahuzac, F. Carlier, M. de Frutos, J. Leygnier, J.Ph. Roux, A. Sarfati: J. Phys. II **2**, 971 (1992)
42 T. Reiners, H. Haberland: Phys. Rev. Lett. **77**, 96 (1996)
43 U. Kreibig, M. Vollmer: *Optical Properties of Metal Clusters* (Springer, Berlin, Heidelberg 1995)
44 W. Ekardt: Phys. Rev. B **65**, 6360 (1985)
45 B. Wästberg, A. Rosén: Z. Phys. D **18**, 267 (1991)
46 M. Koskinen, M. Manninen: Phys. Rev. B **54**, 14 796 (1996)
47 O. Frank, J.-M. Rost: Chem. Phys. Lett. **271**, 367 (1997)