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COMMUNICATIONS

Photoelectron spectra of the alkali metal cluster anions: $\text{Na}_{n=2-5}^-$, $\text{K}_{n=2-7}^-$, $\text{Rb}_{n=2-3}^-$, and $\text{Cs}_{n=2-3}^-$

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(Received 6 June 1989; accepted 12 July 1989)

The photoelectron spectra of a variety of transition metal and semimetal cluster anions have been reported in recent years.¹⁻³ Here, we present the photoelectron spectra of the alkali metal cluster anions: $\text{Na}_{n=2-5}^-$, $\text{K}_{n=2-7}^-$, $\text{Rb}_{n=2-3}^-$, and $\text{Cs}_{n=2-3}^-$. Since alkali atoms have hydrogenic electronic structures and since alkali metals are the simplest of metals, alkali metal clusters are expected to exhibit the least complicated electronic structures among metal clusters. While several theoretical studies⁴⁻¹² of neutral alkali clusters have been reported, there have been relatively few theoretical treatments involving their anions.¹³⁻²¹ Likewise, while experimental studies²²⁻²⁸ relative to neutral alkali clusters abound, we know of only one observation²⁹ of alkali cluster anions ($\text{Na}_{n=2-4}^-$ due to sputtering) previous to this report.

Negative ion photoelectron spectroscopy is conducted by crossing a mass selected beam of negative ions with a fixed frequency laser beam and energy analyzing the resultant photodetached electrons.³⁰ Alkali cluster anions were generated with a high-temperature supersonic expansion ion source, in which several torr of alkali metal vapor were coexpanded with a few hundred torr of argon. Outside the nozzle, in the presence of a magnetic field, a negatively biased hot filament injected relatively low energy electrons directly into the expanding jet, producing alkali metal cluster anions.

The photoelectron spectra of $\text{Na}_{n=2-5}^-$, $\text{K}_{n=2-7}^-$, $\text{Rb}_{n=2-3}^-$, and $\text{Cs}_{n=2-3}^-$, which were recorded with 2.540 eV photons, are presented in Fig 1. These spectra are highly structured, individual peaks arising due to photodetachment transitions between the ground electronic states of the cluster anions and the ground and various excited electronic states of their corresponding *neutral* clusters. Analysis of these spectra yields, as a function of cluster size, vertical detachment energies (VDE's) and adiabatic electron affinities (EA_a 's) (see Table I) as well as energy splittings between the low-lying electronic states of the neutral clusters (at the geometries of their corresponding anions).

We have assigned the electronic transitions observed in the alkali dimer anion (M_2^-) spectra, guidance having been provided by available optical data and theoretical calcula-

tions.⁹ In the spectra of Na_2^- and K_2^- , origin transitions within the $X, M_2 \leftarrow X, M_2^-$ bands were located using literature values for the $A \ ^1\Sigma_u \rightarrow X \ ^1\Sigma_g$ transition energies of Na_2 and K_2 .^{25,26} This provided reliable determinations of the EA_a 's for these species as well as a firm basis for determining the EA_a 's of Rb_2 and Cs_2 . These values for the dimer EA_a 's are consistent with theoretical studies,¹⁶ and they follow the

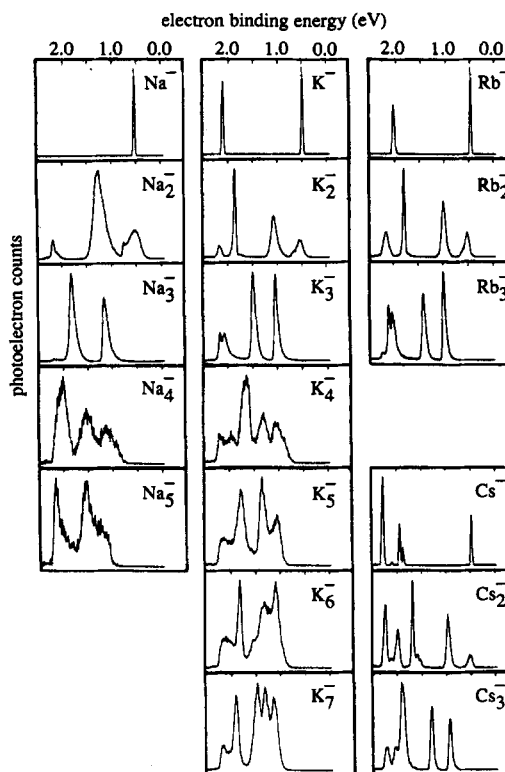


FIG. 1. Presented above are the photoelectron spectra of the alkali metal cluster anions: $\text{Na}_{n=2-5}^-$, $\text{K}_{n=2-7}^-$, $\text{Rb}_{n=2-3}^-$, and $\text{Cs}_{n=2-3}^-$. These spectra were recorded with an instrumental resolution of 30 meV, a photon energy of 2.540 eV, and mass selected ion currents ranging from a few to several hundred picoamperes. The photoelectron spectra of the alkali atomic anions were used as calibrants, and these are included here for comparison.

TABLE I. Results of spectral analysis.

Species	Adiabatic electron affinity (eV)	Vertical detachment energy (eV)
Na ₂ ⁻	0.430 ± 0.015	0.543 ± 0.010
Na ₃ ⁻	1.019 ± 0.060	1.158 ± 0.010
Na ₄ ⁻	0.91 ± 0.15	1.145 ± 0.030
Na ₅ ⁻	1.10 ± 0.10	1.20 ± 0.05
K ₂ ⁻	0.493 ± 0.012	0.550 ± 0.010
K ₃ ⁻	0.956 ± 0.050	1.043 ± 0.010
K ₄ ⁻	0.83 ± 0.12	1.048 ± 0.025
K ₅ ⁻	0.95 ± 0.10	1.045 ± 0.022
K ₆ ⁻	0.95 ± 0.10	1.091 ± 0.020
K ₇ ⁻	1.05 ± 0.10	1.140 ± 0.020
Rb ₂ ⁻	0.498 ± 0.015	0.537 ± 0.010
Rb ₃ ⁻	0.920 ± 0.030	0.988 ± 0.010
Cs ₂ ⁻	0.469 ± 0.015	0.511 ± 0.010
Cs ₃ ⁻	0.864 ± 0.030	0.935 ± 0.010

predicted ordering of EA_a magnitudes, Na₂ < K₂ ~ Rb₂ > Cs₂. Using our measured dimer EA_a values in thermochemical cycles, alkali dimer anion bond dissociation energies were also found.

The VDE's of the alkali trimer anions (M₃⁻) have been determined from the peak maxima of their X, M₃ ← X, M₃⁻ bands, and the assignments of the remaining electronic transitions have been guided by available calculations.^{10,11} Due to the large structural difference between neutral alkali trimers (distorted triangles)^{10-12,27} and their anions (thought to be linear),¹⁷⁻¹⁹ the origin transition energies in their photoelectron spectra are expected to differ significantly from the VDEs. In each trimer anion spectrum, we have assigned the origin transition to the abrupt change in slope observed on the low electron binding energy side of its X, M₃ ← X, M₃⁻ band. These assignments are supported by theoretical calculations¹² which allow the energy difference between the VDE and the EA_a to be estimated for Na₃ and K₃. Alkali trimer EA_a's were found to decrease with increasing alkali mass, in agreement with theoretically predicted trends.²⁰

The EA_a's of the larger potassium and sodium clusters have also been determined. An examination of the EA_a data as a function of cluster size reveals two main trends: a gradual increase in EA_a with increasing cluster size, and an odd-even alternation in which clusters containing an odd number of atoms generally have higher EA_a's than even sized ones. Potassium and copper atoms are both s¹ systems. A comparison of EA_a vs n trends for potassium clusters with those for copper clusters^{1,2} reveals quantitatively different, yet strikingly similar qualitative trends. Where comparisons are possible, the photoelectron spectra also show that the low-lying electronic state patterns for both potassium and copper clusters are similar.

In a companion communication, Bonacic-Koutecky *et al.*²¹ report a theoretical study of small neutral and anionic sodium clusters containing up to five atoms. These calculations model our spectra, providing estimates of EA_a's, anion

VDE's, and electronic state splittings of small neutral sodium clusters at the geometries of their anions. Their results are in semiquantitative agreement with ours, and together they provide insight into the electronic structure and geometries of small anionic and neutral metal clusters.

We thank V. Bonacic-Koutecky, J. L. Gole, W. D. Knight, D. M. Lindsay, W. C. Lineberger, R. E. Smalley, and D. G. Truhlar for stimulating discussions. We gratefully acknowledge the support of the National Science Foundation under Grant No. CHE-8511320.

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