Evaporative attachment of slow electrons to metal nanoclusters

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We present a measurement of the abundance mass spectra of $Na^-_{n\sim7\text{-}140}$ cluster ions formed as a result of low-energy (0.1 eV) electron attachment to free clusters. Both the anion (daughter) and the neutral (precursor) cluster mass spectra were acquired simultaneously, making it possible to investigate their transformations without distortions due to beam variations.

The anion spectrum revealed significant restructuring with respect to the neutral precursors, including a downshift in the shell-closing magic numbers, as well as strong changes in the relative intensities of open-shell peaks. Importantly, the latter effect cannot be explained by a simple pattern shift by one electron number, and requires an accurate treatment.

The restructuring of cluster abundances was analyzed on the basis of a three-stage evaporative attachment picture: (1) electron capture by the polarization potential of the cluster; (2) prompt dissipation of electron attachment energy into the internal vibrational degrees of freedom (cluster heating); followed by (3) evaporative cooling. The last stage, comprising a cascade of monomer and dimer evaporations, was described within the statistical evaporative framework. Convoluting the calculated evaporation chains with the mass spectra of the neutral precursors, we obtained detailed agreement with the experimental data without any adjustable parameters. Furthermore, being sensitive to the cluster dissociation energies, the data verified that the prior literature dimer binding energies need to be corrected by ≈25%.

Thus a complete description of the full process of evaporative electron attachment to metal clusters has been established. The results demonstrate that slow-electron capture offers a useful window into the polarization, statistical and binding properties of nanoclusters. Conversely, they emphasize that in interpreting charge-capture and charge-transfer reactions involving clusters it is essential to account for accompanying evaporative dynamics.

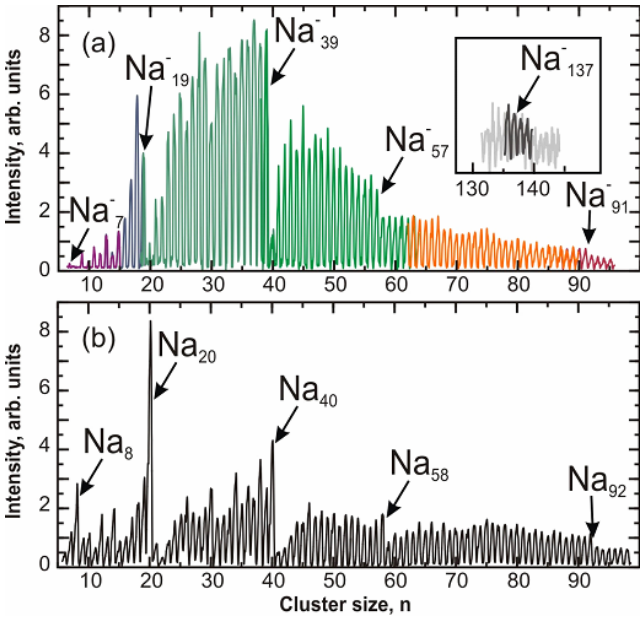

Figure 1: Mass spectra of the electron attachment products (a) and the precursor beam (b)..