BEAM DEPLETION SPECTRA OF K ATOMS ATTACHED TO Ar CLUSTERS. EXPERIMENTAL MEASUREMENTS AND QUANTUM-CHEMISTRY CALCULATIONS

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We have measured beam depletion spectra of potassium atoms and oligomers formed on large argon clusters via the pick-up technique. Unlike helium droplets, where spectral shifts and broadening induced by the droplet are small, unambiguous assignment of the transitions observed in argon (a stronger perturber causing correspondingly broader peaks and larger spectral shifts) is difficult. We tentatively assign the transitions based both on their position, and on their order of appearance as the dopant pressure in the pick-up cell is increased. Of particular interest is what we believe to be the transition already observed in gas-phase pump-probe photoionization experiments[a] then assigned to a transition to a dissociative state (the so called B-state) of the doublet potassium trimer. To corroborate the assignment we computed the ground-state potential energy surface [QCISD(T) level] and vertical excitation energies (CASSCF level) of the doublet potassium trimer, which we also compare to the corresponding spectra, suitably energy-scaled, of the doublet sodium trimer.

[a] H. Ruppe, S. Rutz, E. Schreiber, and L. Wöste, *Chem. Phys. Lett.*, **257,** 356 (1996).